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Editorial Policy

Photographic Science and Engineering is dedicated to the advancement of the knowledge and application of photography and other directly related sciences. Its pages are open to all who wish to report on new studies dealing with the theory of photosensitive systems, the design of photographic instruments and apparatus useful in the treatment of photographic materials, photographic optics and illuminants, the use of photography for scientific or engineering measurement or recording, and photographic instrumentation and data recording. Only original papers should be submitted except on special invitation.

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Graphs, charts, and other line illustrations should conform to good usage such as given in the American Standards Association Document Y-15, "A Guide for Preparing Technical Illustrations for Publication and Projection." Continuous-tone photographs should be made on 8 by 10-inch glossy paper and should show pertinent image detail sufficiently clearly to permit reduction to fit a 3-inch column in this journal. All illustrations should be numbered in soft blue pencil on the back to correspond with captions typed on a separate page. Tables should also be submitted on separate pages appropriately identified. An abstract should accompany each manuscript.

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DEDICATION

For almost forty years, Louis Philippe Clerc's monthly journal, *Science et industries photographiques*, has covered the world literature of photographic science and technology in unique fashion. His masterly résumés concentrated a maximum of information into a minimum of words. It was seldom indeed that any paper in the scientific or technical fields of photography escaped his attention.

The production of *Science et industries photographiques* in itself was an astonishing achievement for one man, for L. P. Clerc wrote without assistance by far the major portion of the technical résumés it contained and he translated into French numerous original papers which had been submitted in other languages for publication in his journal. But this was only part of his work. For many years he also was Editor-in-Chief of *Le Procédé*, translator of many of the articles published therein, and author of the review section. He made important original contributions to the fields of graphic arts and aerial photography. He taught physics and chemistry, as applied to the graphic arts, at l'École Estienne, and lectured on photographic photometry and photographic theory at l'Institut d'Optique. He founded and for many years directed a technical school of photography and cinematography in Paris. He took an active part in the organization of meetings of the International Congresses of Photography from 1900 on, edited the proceedings of the fifth, sixth, and ninth congresses, and published, as a special volume of *Science et industries photographiques*, the papers presented at the postwar International Conference held in Paris in 1951, supplying when needed the translations into French. Somehow, with all these activities, Monsieur Clerc found time to translate several books, to write numerous original articles, and to write some twenty books, including the comprehensive *La Technique Photographique*, which has gone through six French editions and has been translated into several languages.

The great editor, scholar, teacher, and master of the literature is gone, but his monumental writings remain as a source of information for research workers, students, and educators for years to come. The editors of *Photographic Science and Engineering* are proud to dedicate the present issue to the memory of this remarkable man, who died September 7, 1959, at the age of 84.

Other details of Monsieur Clerc's life may be found in the December 1958 issue of *Photographic Science and Engineering*, p. 185; in *Photographic Engineering*, Vol. 6, No. 2, pp. 132–34; in the October 1952 issue of the *PSA Journal*, p. 581; and in the October 1959 issue of *Science et industries photographiques*, Vol. 30, pp. 353–56.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 3, Number 6, November-December 1959

Experimental Studies of the Mode of Action of Sensitizing Impurities in Thin Crystals of Silver Bromide

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An understanding of the behavior of impurities in silver bromide as traps for electrons and positive holes, under conditions which closely match those of photographic practice, is important in the development of the theory of photographic sensitivity. Thin, single crystals of silver bromide, made according to the methods of Mitchell and co-workers, appear to present a suitable system for the investigation of trapping phenomena. Exposure of these crystals to ultraviolet radiation, which is absorbed very near the surface of incidence, produces various image effects which must be attributed to the diffusion of centers deep into the crystal. Latent-image centers which appear at sites remote from the absorption layer seem to be formed by diffusion of electrons; similarly, bleaching effects of exposure on internal latent-fog centers or on dye adsorbed to the unexposed surface indicate diffusion of positive holes. Impurities introduced into the crystal affect the relative production of latent-image centers and of bleached centers according to their ability to trap electrons or positive holes. When the impurity can be introduced in the interior of the crystal in the form of a layer, trapping effects can be observed especially clearly. A layer of silver sulfide so introduced is found to trap both electrons and positive holes, at low as well as at high exposure levels. A layer of ammonium chloroiridite acts essentially as a trap for positive holes. Trapping effects correlated with the introduction of cadmium ion in the crystal are also described.

It is well known that very pure crystals of silver halide show little or no photographic sensitivity, and that sensitivity can be induced by introducing traces of appropriate impurities into the crystal. A main function of these impurity centers is to prevent the recombination of the photoelectrons and positive holes formed in the crystal by the primary absorption of light. Gurney and Mott[1] considered that the sensitivity centers of silver sulfide, which were shown by Sheppard to be associated with high sensitivity of photographic emulsions, acted as traps for electrons, and that the trapped electrons, by combining with interstitial silver ions, formed silver atoms which were incorporated into the particle of reduced silver constituting the latent-image center. More recently, Mitchell,[2] while retaining the Gurney-Mott principles of temporally separate electronic and ionic processes, has revised the details of the trapping processes considered by earlier investigators, emphasizing the importance of positive-hole trapping and the specific requirements of the traps necessary to secure high photographic sensitivity. According to Mitchell's views, an adsorbed silver sulfide molecule introduced on the surface of a grain during chemical sensitization functions by first capturing a positive hole. The positive charge formerly carried by the free hole now appears as a localized, positively charged adsorbed Ag_2S^+ molecule. In order that this localized positive charge may not act as a recombination center for an electron, rendering the electron unable to participate in the formation of a latent-image center, the charge must be lost before an electron approaches the sulfide site. This can happen through the migration of an interstitial silver ion from the site. The silver ion is then available for combination with an electron to initiate, or participate in, the formation of a latent-image center.

In the present state of development of the theory of photographic sensitivity it would therefore seem important to secure as direct information as possible on the trapping properties of impurities of photographic interest, preferably under conditions which match as nearly as possible those of a normal photographic exposure. The object of the present communication is to show how such information can be obtained experimentally for certain types of impurity centers by observing the effect of the impurity on developed images which can be formed in the interior of sheet crystals of silver bromide and on the surface of the crystal remote from the exposed surface.

The material used in these experiments was silver bromide in the form of sheet crystals, about 1 cm square and from 15–100 μ thick, made from the melt by the methods described by Mitchell and his co-workers.[3,4] Exposure of such crystals to ultraviolet radiation generates latent-image centers deep within the crystal at sites to which radiation cannot penetrate with significant intensity.[4–6] These cen-

Presented at the National Conference, Chicago, 29 October 1959. Communication No. 2048 from the Kodak Research Laboratories, received 21 August 1959.

ters can be uncovered by a graded etching procedure which, in one operation, removes layers of different thickness from the crystal, with the ultimate formation of a sloping surface which cuts through the original crystal from front to rear. If the exposure of the original crystal is made through a narrow slit, development after etching yields a visible, slitlike silver image along the sloping surface, the optical density of which, at points along the direction of the slit, measures the corresponding concentration of latent-image centers at points of different depth from the original surface.[5,6]

Besides being formed deep in the interior of a sheet crystal exposed to nonpenetrating radiation, latent image can also be formed on the rear unexposed surface of such a crystal, provided this surface is chemically sensitized. Imagewise bleaching effects, for example, of latent-fog centers, can also be observed on the rear surface after exposure of the front to ultraviolet radiation; positive images are then formed on the rear surface.

The latent-image particles and the bleaching effects produced in parts of these crystals remote from the illuminated zone must originate in centers, formed by direct absorption of radiation near the surface of incidence, which diffuse into the interior and, ultimately, completely across to the rear surface. The available facts seem consistent with the supposition that the diffusing entities are electrons and positive holes,[6] the electrons ultimately combining with silver ions at appropriate sites to form latent-image centers, and the positive holes attacking already existing latent-image and latent-fog centers throughout the crystal, or dye molecules adsorbed to the rear surface. Preliminary experiments performed with the cooperation of R. W. Tyler, of these Laboratories, on the effect of electric fields applied during exposure on the depth of the internal images, seem to confirm that the latent-image-forming diffusing centers are of electronic nature. When a pulsed field of short duration, synchronized with a flash exposure, similar to those employed by Hamilton, Hamm, and Brady,[7,8] was applied in such a direction as to retain photoelectrons near the surface of incidence, the depth to which internal latent image was found within the crystal was diminished. Correspondingly, internal bleaching effects can very probably be ascribed to the diffusion of positive holes into the interior, conclusive evidence for which, in crystalline silver halides, is furnished by the increase in dark conductivity observed when these crystals are immersed in an atmosphere of the corresponding halogen gas.[9–11]

The image effects in the interior and on the rear surface of exposed sheet crystals of silver bromide offer a means of studying the nature of the trapping behavior of foreign centers introduced into the interior or on the surface of silver halide crystals. If the material is uniformly distributed throughout the crystal, changes in the ratio of latent-image production to bleaching effects caused by the impurity will give information on the trapping capacity of the impurity centers for electrons or for positive holes. Similarly, the effect of a layer of the impurity introduced within the crystalline sheet, as described later in this communication, on the image effects in the part of the crystal below the layer, indicates the trapping behavior of the foreign material with respect to electrons and positive holes.

Effect of Trace Amounts of Iron on Internal Sensitivity

It will be convenient first to describe the conditions under which one can observe at will effects concerned with latent-image formation or with the bleaching caused by positive holes within the crystal or at the rear surface. It has been found that a trace of ionic iron (a few parts in 10 million) considerably influences the formation of latent image deep within the crystal, without producing noticeable effects on surface sensitivity or on the internal sensitivity down to about 20 μ from the surface. The appearance of developable latent image down to distances of 40 to 50 μ from the front surface of unannealed crystals is characteristic of material which contains a few tenths part of ionic iron per million; while in the purest crystals which we have prepared, in which the iron, estimated spectroscopically, is reduced to quantities insignificantly different from the spectroscopic lower limit (about 0.05 part per million), internal latent image can be found to a distance of about 20 μ from the surface of unannealed crystals exposed to ultraviolet (nonpenetrating) radiation. If the distribution in depth of internal image in very pure crystals is examined with the use of a development procedure which produces fog on the surface formed by etching, developable latent image is found to depths of about 20 μ from the original

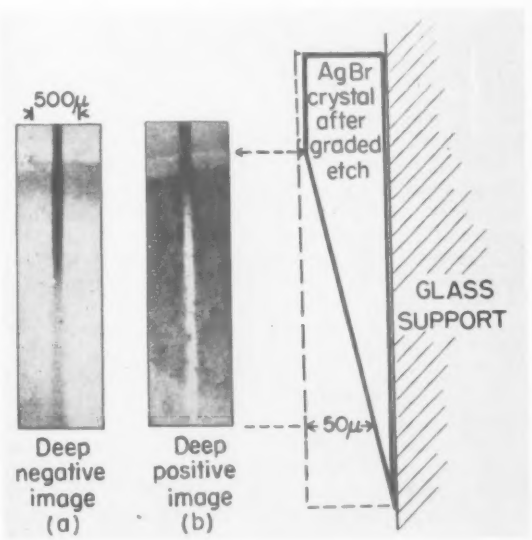

Fig. 1. Developed negative and positive internal images formed from centers which diffused from front to rear of (a) silver bromide containing a trace of iron, (b) very pure silver bromide.

surface, while at greater depths, a positive image is formed against the fog background, by imagewise bleaching of latent-fog centers in the projection of the illuminated area within the crystal. The deep internal images, developed in (a) sheet crystals containing a trace of ionic iron and in (b) very pure crystals, are illustrated in Fig. 1. The view of the images in Fig. 1 is from above, looking down on the sloping surfaces formed by the graded etching. The depths from the original surface at which the latent image corresponding to various points along the slit-like, developed image was formed are indicated in the sketch on the right, showing a section through the crystal perpendicular to the surface of incidence before and after etching, the dotted lines enclosing the parts etched away. In (a), developable latent image was formed throughout the crystal, which exceeded 50 μ in thickness, while in (b), developable latent image was formed immediately below the surface of incidence and for about 20 μ into the crystal, but the deeper image is a positive against the fog background, and was formed by the attack of latent-fog centers by positive holes which diffused into the interior of the crystal.

When, therefore, the distribution of positive holes, as revealed by bleaching effects, is under study, the purest crystals available are used; if the distribution of latent-image centers formed by diffusion of electrons deep within the crystal is of interest, crystals containing a trace of ionic iron are used.

Secondary Image Effects in Unexposed Surface of Sheet Crystals

Image-forming centers may diffuse completely across the crystal to the unexposed surface. If the rear surface is not chemically sensitized, no developable latent image is formed there as a result of exposing the other side, but if, before exposure, the rear surface is chemically sensitized by treatment with compounds from which an adsorbed layer of silver sulfide can be formed, developable latent image may be formed, whether the exposed surface is sensitized or not. Similarly, conditions may be chosen under which, by exposing the front surface, bleaching of developable fog centers or of latent image, preformed by direct exposure of the rear surface, may occur at this surface. Images formed on the rear surface of an exposed crystal by diffusion of centers from the absorption zone may be conveniently termed "secondary images," in contrast to primary images formed at a surface directly exposed to radiation. Secondary latent image is most readily observed in sheet crystals containing a trace of ionic iron; in such crystals, exposures of 0.05 sec and upward, at an incident intensity of radiation of wavelength 365 mμ of about 10^{15} quanta cm^{-2} sec^{-1} may form developable latent image in crystals up to 50 μ thick. In very pure crystals up to 20 μ thick, secondary latent image may be formed by a 5-sec exposure of the opposite face to an intensity of 10^{15} quanta cm^{-2} sec^{-1}, but in thicker crystals, secondary positive images against a fog background (produced by prolonged development of a heavily sensitized rear surface) were formed by exposing the opposite face. The secondary effects caused by long exposure of very pure crystals of any thickness were always bleaching effects.

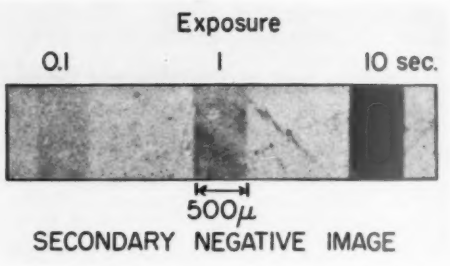

Fig. 2. Secondary negative images formed on a sensitized surface of a sheet crystal by exposing the other side to ultraviolet radiation.

Developed secondary negative images on the rear surface of a sheet crystal, 20 μ thick, of silver bromide containing a trace of iron are illustrated in Fig. 2, which shows the effect of the diffusion of electrons from near the front surface and their incorporation into latent-image centers at the rear. Both sides of the crystal were chemically sensitized by immersion for 2.5 min in a solution of sodium aurodithiosulfate, along with ammonium chloroiridite in 0.5% inert gelatin containing 20 mg/liter of the reagents, adjusted to pH 7.5 and 45°C.[12] One side of the crystal was exposed to radiation of wavelength 365 mμ at an incident intensity of 10^{15} quanta cm^{-2} sec^{-1} for various times through vertical slits, and then the crystal was mounted, exposed side down, on a glass plate, which was immersed in the developing solution, *p*-methylaminophenol–ascorbic acid developer,[13] for 30 sec. Development was confined to the unexposed surface, on which secondary images appeared, as illustrated in the figure. Parafilm* is convenient for mounting these crystals on glass.

By exposing a sensitized surface of a sheet crystal through various thicknesses of silver bromide filter layers, it can be shown that in the exposure times used to form the secondary images, no radiation of wavelength 365 mμ effective in forming latent image can penetrate beyond about 10 μ of silver bromide. The secondary images in Fig. 2 must be formed by diffusion of image-forming centers from the illuminated zone near the surface.

The intensification of a feeble primary latent image on one surface of a sheet crystal by an exposure on the other also was demonstrated. One surface (B) of a sheet 19 μ thick was chemically sensitized as just described, and a weak primary latent image was formed in this surface by a short exposure, through a vertical slit (0.1 sec at incident intensity 2×10^{14} quanta cm^{-2} sec^{-1} of radiation of wavelength 365 mμ). The other surface (A), unsensitized, was then exposed through a horizontal slit for 100 sec to radiation of the same wavelength and intensity, and surface

* Product of Marathon Corp., Menasha, Wis.

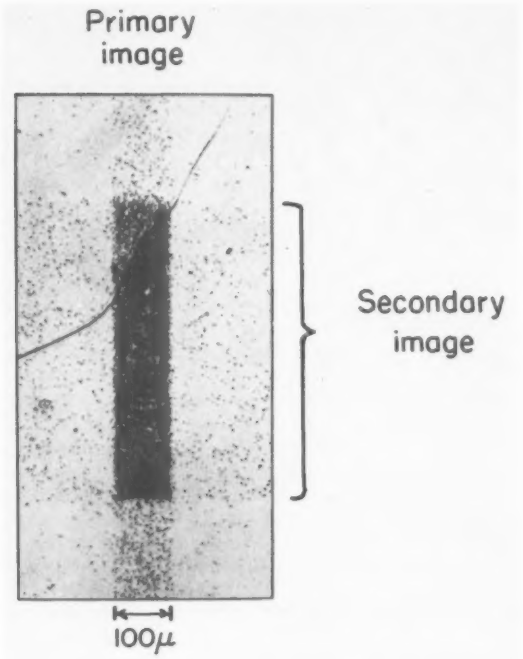

Fig. 3. Intensification of a primary image on the surface of a sheet crystal of silver bromide by electrons which diffuse to this surface as a result of exposing the other side.

B was then developed to produce the result illustrated in Fig. 3. The developed image is much more dense in the region where the primary and secondary images cross than in adjacent regions. Latent subimage centers[14] in surface B, formed by the feeble direct exposure of that surface, but undevelopable under the development conditions used, seem to act as centers for the capture of electrons which diffuse down on illumination of the other surface, with the result that the subimage centers are built up to developable size.

A developed secondary positive image is illustrated in Fig. 4. The crystal, 17 μ thick, was of highly pure material, and was sensitized on one surface by the aurothiosulfate–chloroiridite combination. Primary latent images were first formed by direct exposure of this surface in order to test the sensitization, and then an exposure of 100 sec at an incident intensity of 2×10^{14} quanta cm^{-2} sec^{-1} of radiation of wavelength 365 mμ was applied through a wider horizontal slit on the opposite, unsensitized surface. The sensitized surface was then developed until the developed, primary negative images appeared, along with some fog. The secondary image is the horizontal positive image against the fog background. The exposure which formed the secondary image in this experiment resulted not only in the destruction of latent-fog centers on the rear surface, but also of most of the latent-image centers formed by the 0.5-sec direct exposure on this surface.

Imagewise bleaching of an adsorbed monolayer of the cyanine dye, 5,5′-dichloro-3,3′,9-triethylthiacarbocyanine bromide, on the side of a crystal opposite to the exposed side has also been observed. The crystal used was 35 μ thick. The loss of dye was measured spectrophotometrically by means of the Beckman DU Spectrophotometer. In order to measure the absorption of small areas of the adsorbed dye layer, a much reduced image was projected on the dyed crystal by means of a 16-mm microscope objective, placed behind the exit slit of the monochromator, the strongly diverging light transmitted by the sample being collected by another lens and directed onto the surface of the photoelectric cell. The measurement of the absorption spectra of single monolayers of dye adsorbed to sheet crystals of silver bromide has already been described.[5]

The exposure was applied through a narrow slit to the undyed surface, and absorption measurements were made on the dye in the corresponding region on the opposite side and in regions on this same side lateral to the projection of the illuminated area. After an exposure of 2 hr, 60% of the dye on the unexposed side had been bleached, while in lateral areas the bleaching was much less and vanished at a distance of about 2 mm from the boundaries of the area directly opposite the exposed area.

It is necessary to correct the measured optical densi-

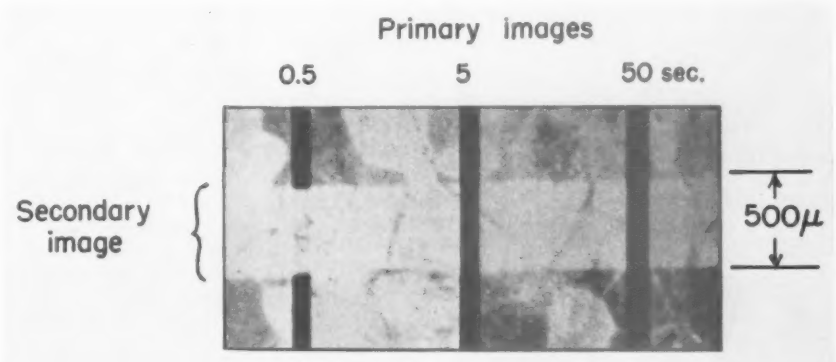

Fig. 4. Secondary positive image in a sheet crystal of silver bromide. Development of the surface opposite to that on which the horizontal exposure was made was continued until the secondary positive image appeared against a fog background. Note also the destruction of the latent-image centers formed by the 0.5-sec vertical exposure.

ties for the density of print-out silver formed during the exposure, mostly near the surface of incidence. Densities were measured at 700 mμ, absorbed by the silver but not by the dye, as well as at the position of the *J*-absorption maximum of the dye, 630 mμ, absorbed by both dye and silver. At the end of the experiment, the dye was removed from the surface by washing with hot methanol, the absorption of the print-out silver was measured as a function of wavelength, and the correction to be applied for the absorption of silver at 630 mμ at any stage of the experiment was made by subtracting the corresponding silver density at 700 mμ multiplied by the ratio of the final silver density at 630 mμ to that at 700 mμ, on the assumption that this ratio did not change during the course of the experiment.

No photolytic silver was formed in lateral areas distant from the slit image by more than a few microns, and in these areas the density of the dye at the position of the *J*-maximum was easily measured. As the measure of the density of the dye in the absence of photolytic silver, the observed density at 630 mμ minus that at 700 mμ was taken. The dye does not absorb radiation of wavelength 700 mμ significantly; hence the observed density at 700 mμ is attributable to scattering and reflection losses of the silver bromide sheet. The error in the correction for reflection and scattering at 630 mμ made on the assumption that these losses are the same as at 700 mμ is quite small.

Although the relative imagewise loss of dye on the rear surface in several mutually confirmatory experiments amounted to a considerable fraction of the dye originally present, the absolute amount of dye destroyed was small, and it is necessary to eliminate stringently possible spurious sources of dye-destruction other than bromine or positive holes which have diffused through the crystal. Precautions were taken to eliminate light reflected from the walls of the room, etc., onto the rear surface of the crystal; since any such light would fall approximately uniformly over the surface, the observed imagewise bleaching excludes the possibility of significant loss of dye by spurious reflected light.

Probably the most serious source of error in the dye-bleaching experiments is the presence of a trace of radiation of wavelength 405 mμ transmitted by the Corning Glass Filter 5860 used to isolate radiation of wavelength 365 mμ from the mercury spectrum. It is therefore necessary to determine how many quanta of radiation of wavelength 405 mμ transmitted by this filter penetrate to the rear surface of a silver bromide sheet 35 μ thick, in 2 hr, the duration of the experiment. The absorption of the dye layer for the violet line of the mercury spectrum is very small, but photobromine produced near the rear surface by this light absorbed by the silver bromide might cause bleaching, which could not then be attributed to diffusion of bromine or positive holes from other regions of the crystal.

For wavelength 405 mμ, the density of the Filter 5860 was determined photometrically and found to be about 3.5, to which the 35 μ thickness of the silver bromide sheet adds a density of 2.5, to make a total density for this wavelength of about 6. The intensity of the violet line in the light emitted by the source is somewhat less than that of the lines of wavelength 365 mμ, which latter, at the surface of incidence of the exposed crystal, was about 10^{14} quanta cm^{-2} sec^{-1}. In 2 hr about 7×10^{11} quanta cm^{-2} of the light of the violet line will penetrate to the rear surface. The number of dye molecules on the surface at the start of the experiment was about 10^{14} cm^{-2}. As already indicated, the dye exhibits very little direct absorption for these quanta, but if every quantum which reached the rear surface formed a bromine atom or a positive hole which attacked a dye molecule, only some 1% of the dye would have disappeared, compared with the observed 60%. Only a small portion of the observed bleaching can therefore be attributed to the penetration of spurious violet light transmitted by the filter to the rear surface.

The transmission of the strong mercury line of wavelength 436 mμ by the Corning Filter 5860 used was quite inappreciable; no light of that wavelength transmitted by the filter could be seen by the dark-adapted eye. The density at the rear surface of the filter-crystal combination for this wavelength must be greater than 8, corresponding to a transmission which could not cause significant bleaching. Similarly, the measured absorption coefficient of silver bromide at 365 mμ[15] indicates that the density of a crystal 35 μ thick for this wavelength is 9, corresponding to quite insignificant penetration to the rear surface. The observed dye-bleaching therefore appears without doubt to be caused by centers which diffuse from sites within the crystal to the dyed surface.

The imagewise bleaching of dye on the side opposite the exposed side of a silver bromide sheet is considerably less sharp than the corresponding imagewise bleaching of latent-image centers. The time required for the dye-bleaching is many times greater than those required to form secondary positive images by the bleaching of latent-fog centers, and the spread of dye-bleaching from the area directly opposite the exposed area on the other side of the crystal is probably the result of diffusion of bromine along the rear surface. Similarly, the solarization of primary images formed by prolonged exposures spreads considerably beyond the illuminated area, indicating lateral diffusion of photobromine along the surface of incidence.

As an example of the information to be obtained from observations on secondary images on the trapping behavior of impurity centers added to the crystal, the effect of cadmium ion on secondary image formation may be described. Crystals of equal thickness, (12 μ) containing 0.1 mole % Cd^{++}, and without Cd^{++}, respectively, chemically sensitized by means of sodium aurodithiosulfate, along with ammonium chloroiridite, on both the surface of incidence and on the opposite surface, were subjected to the same exposure of ultraviolet radiation. Both crystals contained a minute amount of iron. In spite of efforts made to equalize the sensitization for latent-image formation of the surfaces of the crystals with and without cadmium, that of the crystal containing cadmium was lower than that of the other. This

appears, in our experience, to be a general effect of the introduction of cadmium ion. Nevertheless, the density of the secondary developed silver image on the rear surface of the cadmium-containing crystal was considerably greater than that of the secondary image on the rear surface of the crystal without cadmium, indicating considerably more diffusion of electrons across the cadmium-containing crystal. As is well known, an important consequence of introducing divalent cations, such as cadmium ion, into the silver bromide lattice is the creation of a high concentration of silver-ion vacancies. A reasonable conclusion from the increased formation of secondary latent image on the surface of the cadmium-containing crystal, in spite of its intrinsically lower efficiency in forming latent image from the available electrons, is that electrons are transmitted through the cadmium-containing crystal more freely than positive holes, which could be shallowly trapped at the negatively charged, cationic vacancies. Relatively more electrons then reach the rear surface of the cadmium-containing crystal than of the crystal without cadmium, and the lower efficiency of this surface of the cadmium-containing crystal in inducing the build-up of latent-image centers is more than compensated for by the increased number of electrons available at that surface on account of positive-hole trapping by the cationic vacancies in the interior.

Interlayer Effects in Sheet Crystals

A variation of this technique for studying the trapping properties of impurities is to introduce a thin layer of the impurity in the interior of the sheet, parallel to and at a suitable distance below the surface of incidence. For example, by rolling together two sheets mechanically, the surfaces of one or both of which have been chemically sensitized by means of sodium thiosulfate or allylthiourea by standard photographic procedures (but without gelatin), a layer of silver sulfide can be introduced at any convenient depth within the composite sheet so formed. On exposure of this sheet to ultraviolet radiation, electrons and positive holes diffuse into the crystal, and, according to the conditions of exposure and of the trace iron content, form internal latent-image centers or bleach latent-fog centers, the effects of which can be revealed by development of the surface which is cut through the crystal by a graded etch.

The process is illustrated diagrammatically in Fig. 5, which refers to sections of composite sheet crystals formed as just described, cut through the crystal perpendicular to the surface of incidence. The upper sheet, which serves as the experimental "control," is made by rolling together two thinner sheets whose surfaces have not been treated with sensitizer, while the lower sheet is made by rolling together similar sheets of silver bromide, placing in contact surfaces which have been chemically sensitized in some way. The junction in the composite sheet is indicated by the line in the middle, thin in the control sheet and heavy in the sheet containing the interlayer of impurity. For illustration, suppose that the sensitizing

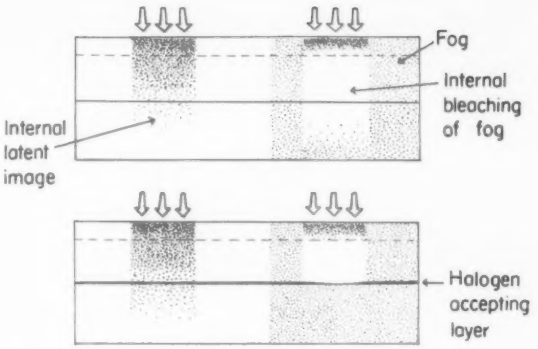

Fig. 5. Effects of unsensitized and sensitized junctions formed within composite sheets of silver bromide on the diffusion of image-forming centers (diagrammatic). Sections of the sheets are drawn, perpendicular to the surface of incidence. The left side of the diagram refers to silver bromide containing a trace of iron, to show diffusion of electrons; the right side refers to very pure silver bromide, to show diffusion of positive holes. The upper crystal contains an unsensitized junction, which interferes with the diffusion of neither electrons nor holes; the lower contains a junction which acts as a trap for positive holes but not for electrons.

impurity acts solely by trapping positive holes. The left half of each composite sheet in the diagram refers to silver bromide containing a trace of ionic iron, in which, as already explained, exposure of the surface readily produces latent-image centers deep in the interior. The material on the right of the diagram is supposed to be very pure, and in the interior of this material latent-fog centers are destroyed by positive holes which diffuse down from the absorption layer near the surface of incidence.

If the sensitizing material in the interlayer in the lower composite sheet in Fig. 5 does not readily trap electrons, the interlayer will not interfere with the diffusion of electrons into the lower parts of the sheet, and, after appropriate etching and development, a negative image will be found extending to about the same depth below the junction as in the control sheet. In the composite sheets of very pure silver bromide, positive holes will be able to cross the junction in the control sheet, but not cross the junction containing the trapping impurity, with a consequent diminution of the bleaching of the fog centers below the interlayer of the lower composite sheet in the diagram. After graded etching and development into fog, the positive image resulting from the attack of latent-fog centers will be absent or weak in the part of the sheet below the interlayer, compared with the image in the corresponding part of the control sheet. Moreover, the trapping of holes by the impurity may cause a chemical alteration of the impurity centers, shown in the diagram by a thinning of the line representing the junction in the lower crystal, in the region affected by the exposure.

In this illustration of the effects on developed internal image to be anticipated as a result of introducing the trapping interlayer into the sheet, it has been tacitly assumed that a junction in the composite

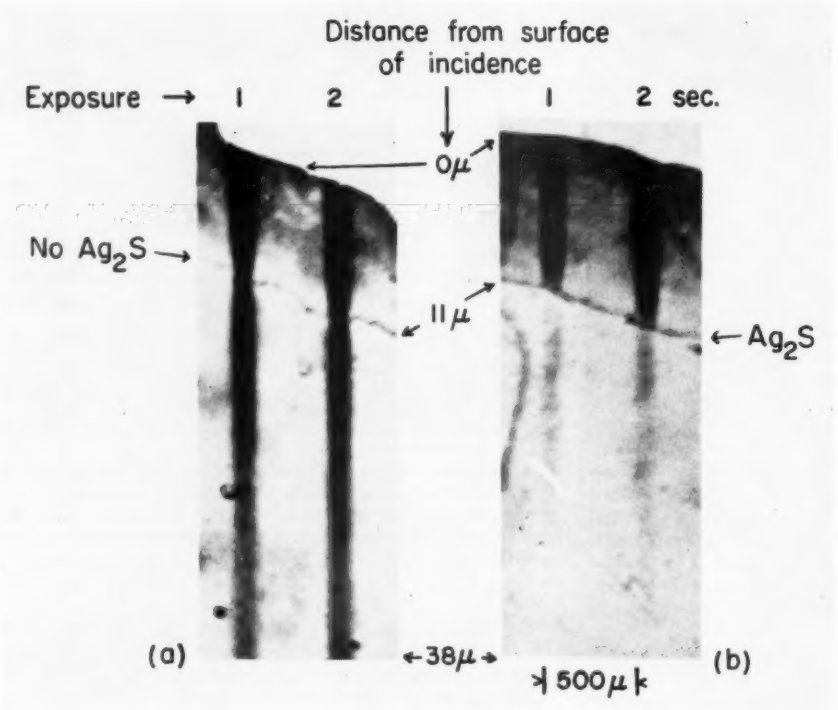

Fig. 6. (a) Transmission of electrons through an unsensitized junction in a control composite sheet containing a trace of iron.
(b) Trapping of electrons in a silver sulfide interlayer in a composite sheet of silver bromide containing a trace of iron.

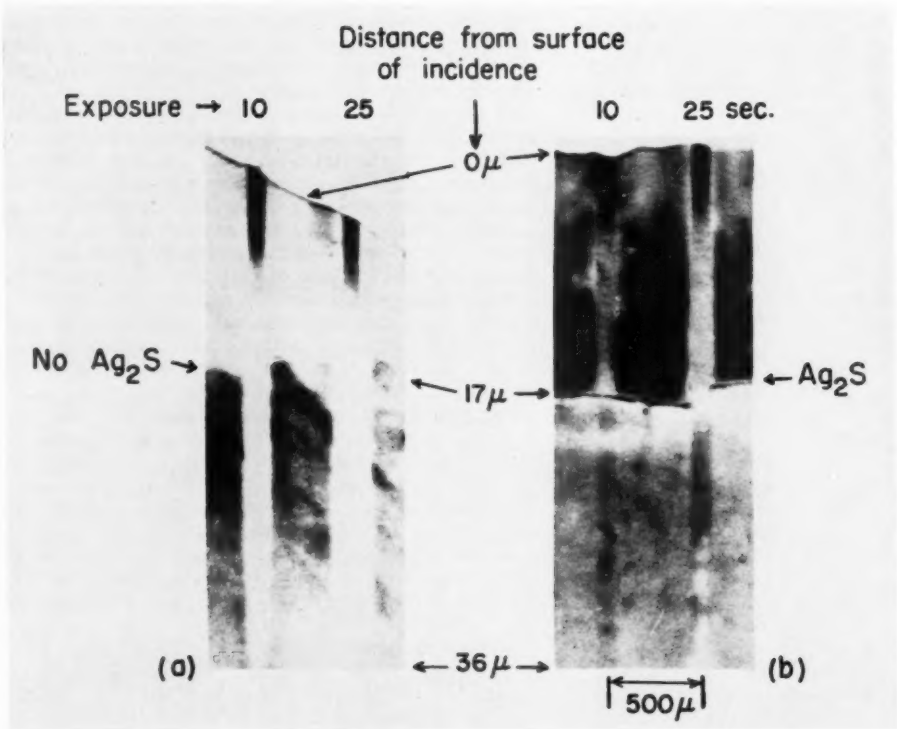

Fig. 7. (a) Transmission of positive holes through an unsensitized junction in a control composite sheet of very pure silver bromide.
(b) Trapping of positive holes in a silver sulfide interlayer in a composite sheet of very pure silver bromide.

sheet made by rolling together two untreated surfaces of silver bromide would not seriously influence the diffusion of electrons or positive holes across the boundary. That this is true for electrons is shown in Fig. 6a, which shows the developed image formed in the surface which, after graded etching, cuts through a control crystal from front to rear. There is no great effect of the junction on the formation of developable image in the regions of the sheet below the junction. The crystal imperfections, which are undoubtedly introduced by the rolling operation, do not appear, in a carefully made junction, to be greatly more efficient as traps for electrons than the dislocations and other imperfections scattered throughout the volume of the unannealed crystals.

In the same way, Fig. 7a shows that the junction formed by rolling together two untreated sheets of very pure silver bromide allows ready transmission of positive holes.

Careful rolling was found to produce a relatively high yield of satisfactory junctions for this type of experiment, but in some cases part or all of the junction was imperfect, as shown by observation of interference fringes. Such an imperfect junction, as is to be expected, will trap electrons and interfere with their diffusion across the boundary. Positive holes, however, are found to be readily transmitted by an imperfect junction, provided the junction contains no impurities which can act as traps for positive holes. When a positive hole reaches an air gap at the boundary, it forms first an adsorbed bromine atom; by combination of atoms, molecules are formed which may be desorbed and pass into the gas imprisoned in the gap. They can then redissolve as positive holes, in the part of the composite sheet below the boundary and produce the bleaching effects by which their presence can be recognized.

A number of experiments involving interlayers of silver sulfide, made by treatment of the surfaces rolled together by standard procedures of chemical sensitizing, indicate that both electrons and positive holes are strongly trapped in the silver sulfide layer; when allylthiourea was employed as the sensitizing substance, hole-trapping was observed only after adjustment of the pH to convert the organic compound to silver sulfide. Thus, although allylthiourea is itself a halogen-acceptor, it does not function as an effective trap for positive holes. The trapping of electrons in an interlayer of silver sulfide introduced into a composite sheet of silver bromide containing a trace of iron is illustrated in Fig. 6b; few electrons penetrate the junction and the developed negative image on the etched surface corresponding to points of the original crystal below the sulfide interlayer is relatively light. Similarly, the trapping of positive holes is shown in Fig. 7b. It will be noticed that the position of the interlayer is marked by a line of fog, which is broken in the part of the crystal affected by the longer of the two exposures, and is lighter than in adjacent portions in the part of the crystal affected by the shorter exposure, presumably indicating attack of silver sulfide by the hole-capturing reaction. Moreover, Fig. 7b shows some developed negative image below the junction, of density greater than that of the positive image immediately above the junction.

Although in the deeper parts of this crystal above the junction there is no evidence of the presence of electrons as a result of exposure, electrons, as well as positive holes, must have diffused down to the boundary and some electrons must have penetrated the boundary into the lower part of the sheet, where they were able to form latent-image centers, the holes having been trapped by the sulfide layer. The relative lightness of the developed negative image below the junction indicates that only a few electrons penetrated the boundary as the result of exposures of 10 and 25 sec, so that the observation is not inconsistent with the electron-trapping capacity of the boundary indicated by Fig. 6b.

One of the most interesting results of this type of experiment with silver sulfide interlayers is illustrated in Fig. 8, which shows attack of silver sulfide on the interlayer by positive holes over the whole range of exposures used, from the shortest (0.1 sec), to the longest. This conclusion seems sufficiently important with respect to the theory of chemical sensitization to warrant an adequate description of its experimental basis, which depends on some peculiarities of the process of graded etching of these crystals.

If a sheet crystal containing particles which are strongly adsorbed to silver halide is etched away by solvents, such as concentrated potassium bromide or dilute cyanide solutions, insoluble particles from the upper layers of the crystal which have been dissolved

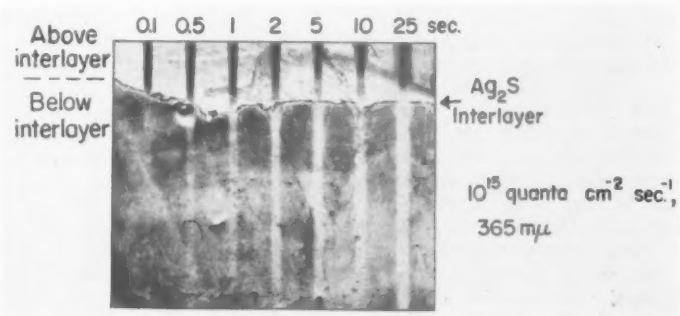

Fig. 8. Attack of a silver sulfide interlayer throughout the whole exposure range. The fog below the interlayer is formed from latent-fog centers which migrate from the silver sulfide interface during etching. The silver sulfide in parts of the interlayer affected indirectly by the exposure is wholly or partly removed by the attack of positive holes which diffuse from near the upper surface, and the spurious fog formed by the etching is of lower density in the parts of the etched surface below the attacked parts of the interlayer than in adjacent parts below unattacked parts of the interlayer.

by the solvent tend to adhere to the newly formed surface.[5,6] Latent-image centers and particles of silver sulfide behave in this way. In studying the distribution of internal latent image, it is necessary to circumvent this effect, otherwise a false estimate will be made on developing the etched surface. Latent-image centers are readily removed by adding potassium ferricyanide to the etching solution, whereupon a clean surface, containing no latent image, is left after etching. To obtain the distribution of latent-image centers at the position within the crystal represented by the etched surface, it is now necessary to dissolve off a thin layer of the crystal by means of the etching solution without the oxidant. The centers are thereby uncovered and become developable. This procedure, while satisfactory for the removal of latent-image centers from the upper parts of the crystal, proved ineffective in removing latent-fog centers which appeared as a consequence of forming a layer of silver sulfide, either on the surface of the crystal or as an interlayer within the crystal. An exposed crystal containing a sulfided surface, treated with developer after an oxidizing etch, yielded neither fog nor image on the surface formed by the etching process, but after the final shallow etch without oxidant, dense fog appeared on those parts of the etched surface corresponding to sites within the crystal below the original sulfided surface. Sulfide specks seem to be carried down from upper layers during the oxidizing etch, adhering to the etched surface. After the oxidizing etch, these particles are protected against development, possibly by a difficultly reducible layer of silver ferrocyanide or ferricyanide. This protection, however, is lost after the final shallow etch with potassium bromide alone, which dissolves the protecting layer, and fog appears on subsequent development.

The fog developed in regions of the crystal below the original sulfided surface, after etching the silver bromide crystal in the manner described, therefore appears to be an artifact originating in the carrying down of developable latent-fog centers from the sulfide layers into regions originally free from fog centers. That this is so is shown particularly clearly by observations on crystals containing a sulfide interlayer. When the etching procedure was applied, starting from the front surface of the original crystal, those parts of the final surface left by the graded etch below the sulfide interlayer were strongly fogged; when the direction of etching was reversed so that the rear surface was first removed, points in the etched surface below the sulfide layer were now free from fog, and dense fog appeared in parts of the etched surface above the sulfide layer. (The part of the composite sheet containing the surface of incidence is regarded "above" the interlayer, and the other part "below.") This dependence of the fog on the direction of etching proves that the latent-fog centers are carried from the sulfide layer into the crystal in the direction of etching, and are not centers produced throughout the crystal during the formation of the sulfide interlayer.

No satisfactory oxidant was found which would solve the difficulty associated with sulfide fog, without seriously attacking internal latent image. It was therefore decided to tolerate the fog, repeating all experiments, first etching from the front to ascertain the true distribution of latent-image centers and of bleached and unbleached latent-fog centers in the part of the composite sheet above the interlayer, then etching from the rear to obtain similar information on the corresponding distributions in parts of the crystal below the interlayer.

As it turned out, it was the effect of exposure on this "spurious fog" which showed that silver sulfide in the interlayer was attacked during exposure at all exposure levels. Figure 8 shows the developed image formed after graded etching from the front (i.e., the exposed surface) of a very pure composite sheet containing a silver sulfide interlayer. The interlayer, 18 μ below the original surface of incidence, is shown as the fogged line which crosses the crystal from left to right. The fog on the etched surface below the interlayer results from the migration of latent-fog centers downwards during the etching process, as just described. If, for any reason, the amount of silver sulfide in the interlayer is diminished, there is a corresponding diminution of the spurious fog. In particular, if, as a result of exposure, silver sulfide is destroyed in the interlayer, the spurious fog, after graded etching and development, will be diminished imagewise against the background which appears in adjacent regions unaffected by the exposure. The positive images in the lower part of the sheet in Fig. 8 are to be interpreted in this way, and are to be distinguished from positive images, such as illustrated in Fig. 7a, formed in unsulfided sheets after graded etching. In Fig. 7a, the developed fog which appears below the join is a true effect originating in fog centers dispersed throughout the lower part of the composite sheet; in unsulfided crystals the difficulties caused by spurious fog are eliminated by the oxidizing etch. Figure 8 shows that attack of silver sulfide during exposure occurs at all exposure levels, and, since positive holes or photobromine in some form are the only photoproducts likely to attack silver sulfide, the evidence is very strong that positive holes are removed by silver sulfide at all exposure levels.

The destruction of silver sulfide during print-out exposures of fast coated emulsions was demonstrated by Hickman[16] in 1927, and by direct analysis of silver sulfide in sulfur-sensitized liquid emulsions exposed to intense illumination, by Sutherns and Loening.[17] In sheet crystals of silver bromide, moreover, Clark and Mitchell[4] showed that the onset of solarization occurred at considerably higher exposures for sulfur-sensitized crystals than for crystals sensitized by the layer of silver oxide or silver formed by heating in air, a result frequently confirmed by the present authors. There seems, therefore, no doubt that silver sulfide reacts with bromine or positive holes at high exposure levels and that the removal of bromine so effected may result in diminished solarization. The present experiments, however, show that positive holes can also be removed by sulfide at low exposures, far below those at which solarization begins to appear, and it would seem very probable that this action plays a significant part in the mechanism of the

sensitization caused by silver sulfide. The interlayer experiments also show that electrons are trapped in, or very near, the layer of sulfide. The present experiments do not show whether electron-trapping and positive-hole trapping by silver sulfide at the surface of silver bromide crystals are completely independent processes, or whether they may be interconnected, as envisaged by Mitchell,[2] but the results are consistent with a mechanism of sensitization by silver sulfide which involves, at low exposures as well as at high, the trapping of positive holes by silver sulfide and the combination of an electron with a silver ion nearby.

Chloroiridite Sensitization

Sensitization of the surface of sheet crystals of silver bromide for the formation of developable latent image by treatment with sodium aurodithiosulfate, along with ammonium chloroiridite, was described by Mitchell and co-workers.[4,12] Recently Steigmann[18] has described the sensitization of certain emulsions by ammonium gold thiocyanate, together with "ammonium iridium chloride." This latter compound is formulated, in Steigmann's communication, as $(NH_4)_2IrCl_6$, ammonium chloroiridate, in which tetravalent iridium is co-ordinated with chloride ions. In ammonium chloroiridite, $(NH_4)_3IrCl_6$, trivalent iridium is co-ordinated with chloride ions. The chloroiridite–chloroiridate couple enters into reversible redox equilibrium involving a one-electron transfer, the normal redox potential of which is 0.87 v.[19] Silver chloroiridate, however, spontaneously decomposes to form silver chloroiridite.[20] This appears to be the explanation of the sensitization conferred by the iridium compound used by Steigmann, and we have, in fact, found that the sensitizing effects of ammonium chloroiridite and ammonium chloroiridate used alone on sheet crystals were practically identical.

Ammonium chloroiridite, acting alone, exerts marked sensitization of the surface of sheet crystals, and the nature of this sensitization was studied by the method of interlayers. One surface of each of two sheets of silver bromide, containing a trace of iron, was treated with ammonium chloroiridite, 1×10^{-5} *M* for 3 min. After rinsing and drying, the treated surfaces were rolled together to form a composite sheet with a chloroiridite interlayer. By the method described in detail for silver sulfide interlayers, the chloroiridite interlayer was found to permit ready diffusion of electrons into the parts of the sheet below the interlayer; chloroiridite is not an efficient trap for electrons. On the other hand, when exposure conditions favorable to internal bleaching were chosen, the chloroiridite layer prevented bleaching very efficiently below the interlayer, indicating efficient positive-hole trapping in the interlayer. Chloroiridite appears therefore to be an example of a sensitizer that functions essentially by the trapping of positive holes. Comparison of the normal redox potential of the silver–silver ion couple, 0.799 v, with that of the chloroiridite–chloroiridate couple, 0.87 v, indicates that chloroiridite will not reduce silver ion efficiently to metallic silver, so that reduction-sensitization, in the sense of Lowe, Jones, and Roberts,[21] is excluded; in fact, ammonium chloroiridite added to silver nitrate forms silver chloroiridite and no reduced silver. The most characteristic feature of the sensitization conferred by chloroiridite to the surface of sheet crystals is the great extension towards high exposure values which can be applied before solarization begins. This is consistent with the conclusion from the interlayer experiments that, in sensitizing, chloroiridite acts essentially as a trap for positive holes.

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A Correlation of the Chemical Structures of Some Triazolopyrimidines with Their Photographic Effects

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The effects of twelve triazolopyrimidines on the fog and speed stability of an experimental silver iodobromide emulsion have been determined. The photographic effects have been correlated with the chemical structures of these compounds. The behaviors have been interpreted by postulating the formation of resonance-stabilized silver salts adsorbed on the grain surfaces. The extent of desensitization by these compounds varied inversely with the solubility of the silver salts and was most pronounced at low-intensity exposures. Several mechanisms of the actions of these compounds are discussed.

Since 1936, triazolopyrimidines* have been suggested as additions to photographic emulsions to inhibit the development of fog.[1–3] That the antifoggant activity of some of these compounds appeared to depend on the formation of stable silver salts or complexes was demonstrated by Birr,[4] who also showed the importance of this characteristic to the stabilizing effects of benzimidazoles, benzotriazoles, and phenylmercaptotetrazole. The reactions of triazolopyrimidines and related heterocyclic compounds with silver ion were studied by Kikuchi and Akiba.[5]

In the present work, the effects of variations in the structure of 5-hydroxy-7-methyl-s-triazolo[2,3-a]pyrimidine (**I**) on aging stability and speed of photographic emulsions were investigated. These compounds were added to the emulsion at the end of the second ripening (sensitization) period. The objective of this work was to determine the specific contribution of the elements of the structure of **I** to its action as a stabilizer.

Experimental Procedure

Twelve triazolopyrimidines were synthesized and added after sensitization and prior to coating (pAg 9.5) to an experimental coarse-grained iodobromide emulsion (1.7% iodide) which had been sensitized with gold and sulfur sensitizers. In this work, the chemical sensitization was extended in order to increase speed and fog, thereby enhancing the effects of the antifoggants. Under these conditions somewhat larger concentrations were required. Each antifoggant was evaluated at three concentrations and with high- and low-intensity x-ray exposures using a Du Pont "Patterson" Par Speed Intensifying Screen having peak emission at 430 mμ. The high- and low-intensity exposures differed by a factor of approximately 100 in intensity; low-intensity exposure time was 10 sec.

A Metol-hydroquinone developer of the following composition was used with intermittent agitation at 20°C for 5 min to develop the exposed emulsions:

3.0	grams	Metol
9.0	grams	Hydroquinone
50.0	grams	Na_2SO_3
50.0	grams	K_2CO_3
4.5	grams	KBr
		Water to make 1 liter

Diffuse visual densities were measured on laboratory densitometers. Speeds were calculated and recorded on an arbitrary linear scale.

Emulsions were stored at 120°F at 65% RH for one week and processed as above in order to obtain the effects of accelerated aging.

Similarly, samples were stored at approximately 50% RH at 70°F to obtain effects of normal aging.

Materials

5-Hydroxy-7-methyl-s-triazolo[2,3-a]pyrimidine (**I**), 6-ethyl-5-hydroxy-7-methyl-s-triazolo[2,3-a]pyrimidine (**II**), 2-ethyl-5-hydroxy-7-methyl-s-triazolo[2,3-a]pyrimidine (**III**), 5-hydroxy-7-*n*-nonyl-s-triazolo[2,3-a]pyrimidine (**IV**), and 7-*n*-heptadecyl-5-hydroxy-s-triazolo[2,3-a]pyrimidine (**V**) were prepared from the appropriate starting materials by the method used by Bülow and Haas[6a] in the synthesis of **I**.

8-Hydroxy-6-methyl-s-triazolo[4,3-b]pyridazine (**VI**) was prepared by the method of Bülow and Haas.[6b]

5,7-Dimethyl-s-triazolo[2,3-a]pyrimidine (**VII**) was prepared by the method of Bülow.[7]

5,7-Dihydroxy-s-triazolo[2,3-a]pyrimidine (**VIII**) was prepared by the method of Heimbach and Kelly.[2]

6-Carbethoxy-5-hydroxy-s-triazolo[2,3-a]pyrimidine (**IX**) was prepared by the method of Reynolds

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* *Editor's note:* These compounds can be, and often are, called triazaindolizines or tetrazaindenes.

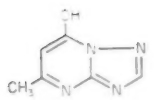
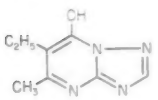
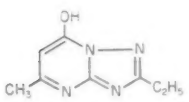
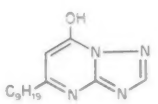
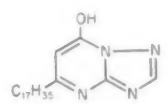
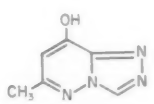
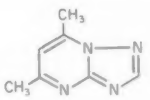
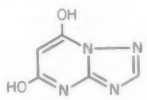
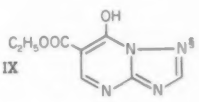
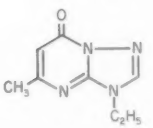
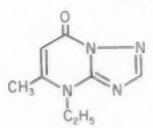
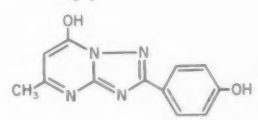
and Segal.[8] The recent work of Allen et al.[9] has established the position of ring junction in I and presented evidence which favors the structural assignment of the pyrimidine ring as shown. The position of ring junction in some of the other compounds in this series has not been established, but can be suggested on the basis of analogy.

1-Ethyl-7-methyl-s-triazolo[2,3-a]pyrimidin-5(1H)-one (**X**), 8-ethyl-7-methyl-s-triazolo[2,3-a]pyrimidin-5(8H)one (**XI**) and 2-*p*-hydroxyphenyl-5-hydroxy-7-methyl-s-triazolo[2,3-a]pyrimidine (**XII**) were prepared and their structures established as indicated in a forthcoming publication.[10]

Results

The effects of these compounds on the stability of emulsion fog during normal aging were found to parallel the results in accelerated aging. For simplicity, and because the latter effects were the larger, only the accelerated aging effects are shown in Table I. In order to normalize the results of many test programs, in each case the fog obtained in the absence of the antifoggant has been taken as 100 and the per cent decrease in fog resulting from the addition of the antifoggant is reported. Similarly, the effects of these compounds on speed are shown as the per cent decrease in speed obtained on a low-intensity exposure of the fresh emulsions. Data indicate pronounced desensitization. Although similar desensitization was also observed at high-intensity exposures of fresh and aged films, the effects were much smaller than those reported in Table I. The speed (linear scale) of

TABLE I — Effects of Triazolopyrimidines on Speed and Fog

Compound	Concentration (mmoles/mole AgBr)	% Decrease in Fog*	% Densensitization†
I 	19.5	61	29
II 	19.5	71	14
III 	19.5	88	30
IV 	5.2	95	88
V 	7.8	94	63
VI 	14.0	17	0
VII 	19.5	0	0
VIII 	19.5	0‡	—
IX 	14.0	89	20
X 	19.5	0	—
XI 	16.0	0	—
XII 	11.0	Fog‖	6

* Fog after accelerated aging for 1 week at 120°F, 65% RH. Fog of emulsion without antifoggant taken as 100%.

† Low-intensity exposures of fresh films. Speed (linear scale) of the control emulsion was taken as 100%. When compounds were inactive as antifoggants, some speed values were not reliable due to the high residual fog and have not been recorded.

‡ This compound increased fresh fog values.

§ The carboxylic acid corresponding to this ester was also evaluated and found to be less effective.

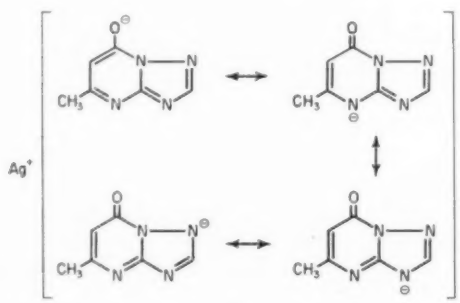
‖ Although fresh fog values were reduced, the results of accelerated aging indicated that this compound increased fog.

the control emulsion was taken as 100%. In general, the reductions in fog and speed increased with increasing concentrations of each test material. The results in Table I are reported for the single concentration indicated.

Discussion

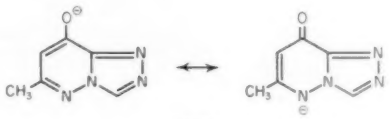
The results in Table I show that, in general, the extent of densensitization increases as the fog decreases. However, significant differences in the behaviors of these compounds are present. All of the compounds having a free hydroxyl group in position 5 in the s-triazolo[2,3-a]pyrimidine nucleus were effective antifoggants, including those having simple alkyl (**I**, **II**, **III**) or carbethoxy (**IX**) substituents. These compounds can be expected to show approximately the same physical and chemical properties since only minor differences occur in the structures. Although substitution of large alkyl groups in position 7 of this nucleus would not be expected to alter significantly the chemical properties of the molecule, large effects on the physical properties can be anticipated. Birr[4] showed that **IV** was a strong desensitizer and that the silver salt of this compound was much less soluble than the silver salt of **I**. He further showed a parallelism between the desensitization of compounds having various alkyl substituents attached to position 7 and the solubility of the corresponding silver salts. The present investigation corroborates the observations made by Birr, since **IV** and **V**, which form insoluble silver salts relative to **I**, gave the strongest desensitization of all the compounds tested.

The importance of salt formation to the activity of these compounds as antifoggants is illustrated in the evaluations of **VII**, **X**, and **XI**. Although complex formation, such as the silver ion-ammonia complex, is possible, none of these compounds can react with silver ion to form a salt. In fact, **X** and **XI** differ from the active compound **I** only in the replacement of the acidic hydrogen by an alkyl group attached to nitrogen. None of these showed activity as an antifoggant or desensitizer. It should be emphasized that the silver salts of compounds such as **I** are best represented as resonance hybrids of structures having the negative charge ascribed to nitrogen as well as oxygen:



I

This has been establisned by the structures of products obtained from the silver salt[3,10] and by other means.[10] These results indicate a large contribution of $N^{\ominus}$ forms to the anion of **I**. This fact appears to be important to the action of **I** as an antifoggant, as illustrated by the behavior of the isomeric compound **VI**. Although similar forms may contribute to the structure of this anion —



VI

the resonance is limited to the pyridazine ring. This material has been reported[6b] to give a ferric chloride test. The evidence suggests that the hydroxyl group in this molecule more closely resembles that of a phenol than does the hydroxyl in **I**. The structures also show that the hydroxyl in **I** can be changed by tautomerism to an amide carbonyl group unlike the hydroxyl in **VI**. These considerations suggest that $N^{\ominus}$ structures do not make a large contribution to the structure of **VI**. The experimental data show that although **VI** forms silver salts,[5] it was only weakly effective as an antifoggant and did not desensitize.

Japanese workers have investigated the effects of some of these compounds in the second ripening reaction.[3] In general, each triazolopyrimidine inhibited the sensitization reactions to an extent which paralleled its tendency to form a silver salt. As in the present work, **VIII** increased fog and **VI** and **VII** were less active than **I**.

The stabilizing action of the salt-forming triazolopyrimidines is best interpreted as an inhibition of those reactions which tend to convert sensitivity centers to developable fog centers on aging. This process is probably similar to that in the second ripening reaction studied by the Japanese workers.[3] The correlation of structures with activities of these compounds suggests that the best protecting action is obtained with salts in which the negative charge in the anion is distributed throughout the molecule by resonance contributions of structures having $N^{\ominus}$ forms. The presence of the adsorbed salt on the surface of the silver halide grain can be expected to interfere with surface reactions — for example, development — thereby resulting in densensitization. The hypothesis that desensitization is produced by retardation of development is supported by the fact that the extent of desensitization increased as the solubility of the silver salt of the antifoggant decreased.[4] Retardation of development by **I** has been demonstrated by Faerman and Simkina.[11] The present observation that desensitization was most pronounced at low-intensity exposures was at first considered to result from a greater inhibition of the development of the surface image than of the internal image. Several reports have indicated that high-intensity exposure produces more internal image than low-intensity

exposure.[12] Thus a greater effect of the adsorbed desensitizer might be expected at low-intensity exposure, since the surface image would represent a larger proportion of the total image. This was verified experimentally by the procedure of Dyba and Smith,[13] using a Metol-isoascorbic acid developer and ferricyanide bleach. However, the external image constituted 86% of the total image at high intensity and 89% at low intensity, indicating the great importance of the external image at both exposures. This fact suggests that development effects are probably inadequate to account for the large variation in desensitization with exposure intensity.

On the other hand, the fresh photographic speed of the control emulsion used in this work decreased 50% on changing from the high-intensity to the low-intensity exposure (low-intensity reciprocity failure). This effect is of the same magnitude as the desensitizations obtained with the strongly active desensitizers and suggests that the desensitization effects may be explained by participation of the desensitizer in the photoelectric mechanism of latent image formation. Such a hypothesis, in which the desensitizer acts during the exposure step, was advanced by A. Hautot and L. Falla.[14] The present work suggests that the adsorbed desensitizers compete favorably with electron traps on the grain surfaces for photoelectrons released during a long low-intensity exposure. The large number of electrons released at high-intensity exposure show less specificity in trapping locations, and proportionately fewer of these are deactivated by the adsorbed desensitizers. West and Carroll[15] reached a similar conclusion in their studies of the effects of desensitizing dyes on the photoconductivity of silver halide grains.

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Action of Organic Stabilizers on a Photographic Emulsion

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Certain organic compounds, commonly reported as photographic emulsion stabilizers, reduce the rate of sensitization of a medium-speed silver bromoiodide emulsion. When added at the beginning of the second digestion, 5-mercapto-1-phenyltetrazole had the greatest retarding action of those studied. Benzotriazole and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were moderately active while 5-nitrobenzimidazole had little effect. Only 5-mercapto-1-phenyltetrazole caused a marked loss of speed when added to the fully sensitized emulsion prior to coating.

Gelatin layers of yellow colloidal silver, print-out silver, and latent-image silver particles were treated with the stabilizers. The effects of stabilizers on the silver particles which catalyze physical development of these model systems were studied. 5-mercapto-1-phenyltetrazole had a much greater inhibiting action than the other three compounds. The similarity between the retarding effects of the stabilizers in both the silver particle systems and the emulsion suggests that the compounds are adsorbed to active centers or partially formed sensitivity specks and prevent their growth.

The photographic journals and patent literature describe many organic compounds which act as antifoggants under conditions of extended development time and as stabilizers to protect the sensitive coatings against fog on aging. As pointed out by Carroll, Hubbard, and Kretchman,[1] the changes that take place during storage may be considered to be a slow continuation of the chemical sensitization process. In the sensitization of a simple emulsion, sensitivity nuclei are formed on the surface of the silver halide crystal during the digestion after washing. These centers are visualized as minute particles of silver and arise from the action of sensitizing substances present in the gelatin. In practical emulsion manufacture, it is not possible to entirely consume all the sensitizers present in commercial gelatins and sensitization may continue at a slow rate even after coating and drying the film. The continuation of this sensitization beyond the region of optimum speed may result in fog.

The rate of sensitization during the second digestion can be regulated by controlling the silver ion concentration. Relatively high values of silver ion result in a rapid rate while low values cause a low rate of sensitization. This rate may be reduced to a low level which is optimum for storage of film by controlling the bromide, as shown by Forsgard.[2] Common organic stabilizer compounds form insoluble silver salts, and therefore lower the silver ion concentration. Matthies and Wendt[3] proposed that stabilizing action resulted when the silver salt solubility was the same or less than the solubility of the silver halide emulsion crystals. Birr[4] has shown that repression of the silver ion concentration, as revealed by potentiometric titration and silver salt solubility studies of common heterocyclic organic stabilizers, correlates well with antifoggant activity.

Stabilizers are adsorbed to the surface of a silver halide crystal as shown by the dye stabilizer replacement studies of James and Vanselow[5] and the crystal growth retardation studies of Birr.[4] The low silver salt solubility and the property of strong adsorption of stabilizers support the concept that a protective hull is formed around the emulsion grain. Mees[6] points out, however, that marked antifoggant action can be obtained by amounts so small that a complete monomolecular layer is impossible and suggests some form of selective adsorption. Koseki[7] has recently determined the minimum amount of organic retarder necessary to reduce the rate of sensitization without causing a speed loss and found that only 5 to 7% of the silver halide crystal surface is covered. He concludes that the stabilizer compounds reduce the catalytic activity of the active centers.

It is proposed here that certain stabilizers may be adsorbed preferentially on the active centers and reduce or destroy the catalytic activity of the speck. This action can be shown by studying the effect of a selected group of compounds when added at the beginning of the second digestion of a photographic silver bromoiodide emulsion. In addition, model experiments were carried out in which the catalytic activity of small silver particles toward physical development was altered by the presence of organic

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stabilizer compounds. Yellow colloidal silver, print-out silver, and latent-image silver were used in the catalysis studies.

Emulsion Experiments

A silver bromoiodide emulsion of neutral type containing 1 mol % iodide was prepared by rapidly adding 1100 ml of 10% (W/V) silver nitrate to a solution of 432 grams KBr, 5.5 grams KI, and 110 grams gelatin in 2300 ml of H_2O at 56°C. The mixture was vigorously agitated during a pause of 10 min, after which a solution of 4400 ml of 10% silver nitrate was added over a period of 7 min; 610 grams dry gelatin were dissolved in the mixture over a period of 15 min; the batch then was chilled, shredded, and washed. A yield of 10 kg of washed noodles was obtained which had a pH of 6.8 and a pAg of 9.25 at 40°C. The silver halide crystals were about 0.6 μ in diameter and had the form of triangular and hexagonal platelets. In the second digestion the emulsion was melted, adjusted to pAg 9.7 with KBr and heated at 57°C. Samples were withdrawn after periods of 30, 45, 60, and 90 min and coated on a film base support at 10 μ thickness. After drying, the films were exposed in a drum-type intensity scale sensitometer using tungsten light filtered to 6000°K and developed 7 min in Ansco Developer A-47. The speed was expressed in mcs^{-1} at net density 0.2.

The 90-min digested emulsion coating was examined for degree of reduction sensitivity by bleaching in an acid dichromate solution composed of 1 gram $K_2Cr_2O_7$ and 7 ml 5*N* H_2SO_4 per liter. The coating was washed 30 min in running water to remove any bromide ions, bleached 15 min at 20°C, washed, dried, exposed, and processed. The bleached film speed was 4. Since the original speed was 16 and the emulsion without digestion had a speed of 2.2, it was concluded that a significant portion of the sensitivity is of the reduction type.

The addition of 5 mg of 5-mercapto-1-phenyltetrazole per kilogram of emulsion at the beginning of the second digestion retarded the rate of sensitization. These data are shown in Table I.

TABLE I

Retarding Action of 5-Mercapto-1-Phenyltetrazole

Digestion time (min)	Control			5 mg 5-mercapto-1-phenyltetrazole per kg emulsion		
	Fog	speed	Gradient	Fog	Speed	Gradient
30	0.06	6.2	0.76	0.04	2.2	0.49
45	0.05	8.8	0.86	0.05	2.9	0.62
60	0.06	11.5	0.99	0.05	5	0.78
90	0.06	15	1.32	0.07	6	0.96

Various amounts of 5-mercapto-1-phenyltetrazole, benzotriazole, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (mp, 278°C) and 5-nitrobenzimidazole were added at the beginning of a 90-min digestion at 57°C. The stabilizer compounds were also added just before coating to an emulsion previously digested for 90 min without additives. The effects of the additives before and after second digestion are summarized in Table II.

TABLE II

Effect of Adding Stabilizers Before and After Second Digestion

		Stabilizers present during sensitization			Stabilizers added after sensitization		
	mg/kg	Fog	Speed	Gradient	Fog	Speed	Gradient
Control		0.06	14.5	1.19	0.06	14.5	1.19
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5	0.07	11.0	1.20	0.06	13.5	1.18
	20	0.06	10.0	1.12	0.06	15.0	1.18
	200	0.06	0.75	0.33	0.07	10.5	1.24
5-mercapto-1-phenyltetrazole	5	0.06	5.8	0.96	0.06	12.0	1.20
	20	0.05	0.43	0.27	0.06	9.0	1.11
Benzotriazole	5	0.07	11.0	1.17	0.06	14.5	1.19
	20	0.06	4.5	0.73	0.07	14.5	1.19
	100	0.06	0.80	0.40	0.07	11.0	1.24
Nitrobenzimidazole	20	0.06	14.5	1.19	0.07	14.5	1.19

Model Experiments with Print-Out Silver

Print-out paper (Ansco Proof Paper) was uniformly exposed to sunlight to a medium density, subsequently fixed by two successive treatments in 7% aqueous ammonia, and then washed. A light density of yellow colloidal silver was obtained. When this paper was immersed in a solution of sodium silver sulfite prepared from 5 grams $AgNO_3$, 30 grams Na_2SO_3, 4 grams ethylenediamine tetraacetic acid trisodium salt in 800 ml H_2O (final pH = 8.3), the initial light yellow was observed to become progressively darker. Solutions of the stabilizers were spotted on the colloidal silver layer and, after drying, were subjected to sodium silver sulfite physical development. It was observed that the deposition of silver was markedly reduced or prevented by the stabilizers. 5-mercapto-1-phenyltetrazole was the most potent and as little as 0.001 mg spread over a 3.5-cm diameter circle inhibited the reaction. Benzotriazole inhibited at the 0.01 mg level while 0.1 mg was required in the case of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 5-nitrobenzimidazole.

Another method was used to demonstrate the restraining action of stabilizers on silver catalyzed physical development. Print-out paper was exposed through a step table and fixed with ammonia as before to give a colloidal silver step wedge. The wedge was bathed for 10 min in a 0.01 mg/ml solution of stabilizer, washed 10 min and developed for 2 hr in the silver sulfite solution. The light yellow step areas of the control became progressively darker as physical development proceeded. The development of the stabilizer-treated strips was inhibited. The resulting densities were plotted (Fig. 1) against the relative log exposure originally given the print-out paper. The mercaptophenyltetrazole had the greatest retarding action while the other compounds had only a moderate effect.

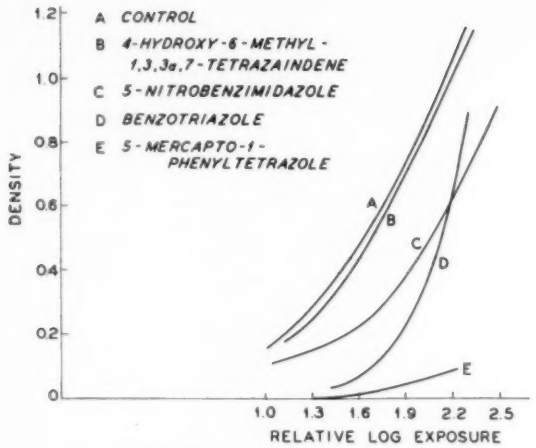

Fig. 1. Effect of stabilizers on the sodium silver sulfite physical development of print-out silver.

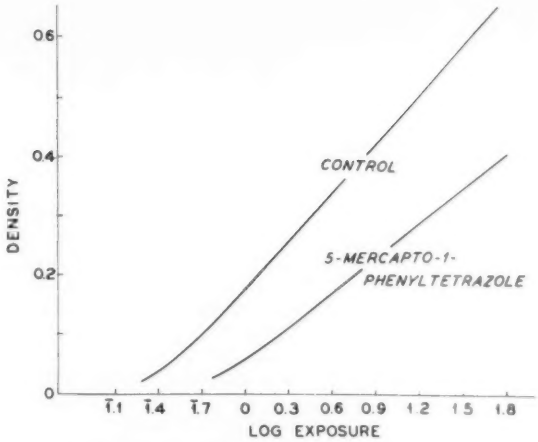

Fig. 2. Effect of 5-mercapto-1-phenyltetrazole on latent image using post-fixation physical development.

Model Experiments with Latent-Image Silver

Strips of the fully sensitized (90-min digestion) emulsion coating were sensitometrically exposed as before and then fixed for 14 min in a solution of 5% $Na_2S_2O_3$ and 0.5% NaOH, washed, and dried. The resulting films were completely clear but contained colloidal silver in the latent-image particle size range. After bathing in stabilizer solutions at 0.1 mg/ml for 10 min and washing for 2 min, the films were developed in a *p*-phenylenediamine physical developer for 20 min. The results, plotted in Fig. 2, again demonstrate the strong retarding effect of the mercaptophenyltetrazole. The tetrazaindene, benzotriazole, and nitrobenzimidazole compounds were inactive.

Model Experiments with Yellow Colloidal Silver

Yellow colloidal silver was prepared according to the method of Perry, Ballard, and Sheppard.[8] One kilogram of the silver noodles was melted, 15 ml of 10% formaldehyde and 1000 ml of a 2% gelatin were added, and the mixture was coated on film base at a thickness of about 3.5 μ. The resulting coating had a light yellow color of density 0.3 and contained 0.49 mg Ag/dm^2.

Spots of stabilizer solutions were placed on the colloidal silver film by spreading 0.3 ml over a 2.2-cm diameter circle. After drying, the specimens were developed in the sodium silver sulfite physical developer for 1.5 hr. The untreated areas increased in density from the original 0.3 to about 3.0, while the treated areas had a lesser density. 5-mercapto-1-phenyltetrazole in a concentration of 0.0001 mg/ml was needed to stop development. The nitrobenzimidazole and tetrazaindene were the least active and 0.1 mg/ml was needed for only a partial inhibition.

In another experiment, stabilizer compounds were added to the melted yellow colloidal silver solution before coating. The quantities added are based on the original silver preparation which contained 2.3 grams of silver per kilogram. After coating, the samples were developed in the sodium silver sulfite developer for 2.5 hr. The densities before and after development are given in Table III. 5-mercapto-1-phenyltetrazole is the most active. Benzotriazole has a moderate retarding action while the tetrazaindene and benzimidazole show little effect.

TABLE III
Effect of Stabilizers on the Physical Development of Colloidal Silver

Additive	Amount mg/kg	Density		
		Before dev	After dev	Difference
Control		0.30	3.28	2.98
4-hydroxy-6-methyl-1,3,3a, 7-tetrazaindene	50	0.31	3.17	2.86
	200	0.31	3.08	2.77
	1000	0.30	2.54	2.24
5-mercapto-1-phenyltetrazole	10	0.30	2.22	1.92
	20	0.34	1.32	0.98
	30	0.30	0.38	0.08
	40	0.25	0.25	0
Benzotriazole	50	0.27	2.85	2.48
	70	0.25	1.75	1.50
	100	0.28	1.15	0.87
5-nitrobenzimidazole	20	0.29	3.18	2.89
	100	0.29	2.94	2.65
	200	0.28	3.05	2.77

Several of the stabilizer colloidal silver coatings of Table III were selected for a development rate study in the sodium silver sulfite physical developer. Figure 3 shows that a low concentration of the mercaptotetrazole retards development while greater amounts of the tetrazaindene and nitrobenzimidazole did not effect development. Benzotriazole had a moderate retarding action in the concentration used.

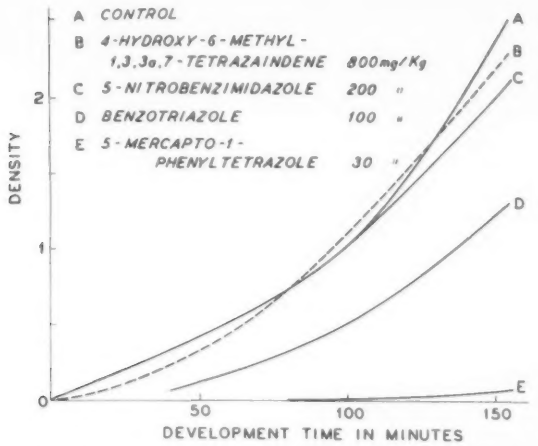

Fig. 3. Effect of stabilizers on the sodium silver sulfite physical development rate of colloidal silver.

Experiments with Colloidal Silver Sulfide

A limited number of experiments were made in which silver sulfide gelatin coatings were treated with a stabilizer and submitted to sodium silver sulfite physical development. In one case, the silver sulfide coating was prepared by bathing the colloidal silver coating, described above, in an aqueous solution of 2.5 grams $Na_2S \cdot 9H_2O$ per liter for 60 hr, followed by washing. Residual silver was removed by bleaching in 1 gram $K_2Cr_2O_7$ and 7 ml $5N$ H_2SO_4 per liter. Spots of 5-mercapto-1-phenyltetrazole were placed on the coating in the same manner as in the colloidal silver experiments and finally subjected to sodium silver sulfite development. The area treated by the tetrazole was unchanged while the original light brown area became progressively darker as development proceeded.

In another experiment, colloidal silver sulfide was prepared by rapidly mixing a solution of 1.7 grams $AgNO_3$ and 25 grams gelatin in 200 ml H_2O with a solution of 2.4 grams $Na_2S \cdot 9H_2O$, and 25 grams gelatin in 200 ml H_2O at 35°C. The resulting brown solution was chilled and shredded, then washed for 3 hr, and finally coated on film base at a thickness of 6 μ. The tetrazole compound was again observed to prevent the increase of density upon sodium silver sulfite physical development.

Discussion

In the medium speed silver bromoiodide emulsion used in this study, organic stabilizers retarded the rate of sensitization during the second digestion. The four compounds selected for this study are reported by Faerman and Pletnev[9] to have the following silver salt solubility products: 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene $1.2 \cdot 10^{-12}$; benzotriazole $3.1 \cdot 10^{-13}$; 5-nitrobenzimidazole $2.2 \cdot 10^{-13}$; 5-mercapto-1-phenyltetrazole $9.3 \cdot 10^{-15}$.

The data of Table I show the strong retarding action of 5-mercapto-1-phenyltetrazole on the rate of sensitization. A comparison of the action of the four compounds investigated was made by adding various amounts to the emulsion, followed by a 90-min digestion. The compounds were also added to the 90-min digested emulsion prior to coating. These data are summarized in Table II. 5-mercapto-1-phenyltetrazole exhibits the strongest retardation of chemical sensitization, benzotriazole a moderate amount, while 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene showed only a slight retardation in the 5 to 20 mg/kg range. When large quantities, such as 100 to 200 mg/kg, are added, the tetrazaindene gives a marked speed loss. 5-nitrobenzimidazole did not retard the rate of sensitization. When the stabilizers are added to the fully sensitized emulsion before coating, the desensitizing action is far less than observed when the compounds are introduced at the beginning of the second digestion. 5-mercapto-1-phenyltetrazole has the greatest desensitizing action on the fully sensitized emulsion while the other compounds show a speed loss only at higher concentrations. The greater retarding effect of the stabilizer compounds on the chemical sensitization must be due to an interference in the growth of sensitivity centers.

Although the compounds all form insoluble silver salts, the quantity present is not sufficient to cause more than a slight change in the pAg of the emulsion. The retardation of chemical sensitization results from either the formation of an insoluble silver stabilizer salt which is adsorbed to the surface of the silver halide crystal or adsorption to an active sensitivity site.

The emulsion used in this study has a significant amount of reduction sensitivity as judged by chromic acid bleaching. Thus, much of the photographic sensitivity may be attributed to silver. Since stabilizer action on silver particles may be involved, the effect of the compounds on the catalytic activity of small silver particles was studied. Model systems were used in which silver particles in the latent image, print out, and yellow colloidal size were treated with the test compounds and finally subjected to physical development. The mercaptotetrazole compound is visualized as being strongly adsorbed on the surface of the silver particle. This surface layer would act as a barrier to the deposition of silver from the physical developer solution. The data in Table III shows that 30 mg of 5-mercapto-1-phenyltetrazole causes inactivation of 2.3 grams of yellow colloidal silver. Using the reported value of 20 mμ for the diameter of yellow colloidal silver, it can be calculated that there may be one molecule of tetrazole adsorbed per 60 sq A of surface. For monomolecular adsorption of 5-phenyl-1-mercaptotetrazole the calculated value for flat-on orientation is 74 sq A, edge on is 71 sq A, and end on is about 50 sq A. This is evidence that complete inhibition of physical development corresponds to the formation of a monomolecular layer of the tetrazole on the colloidal silver particle.

Benzotriazole is less active than the mercaptotetrazole while the tetrazaindene and benzimidazole are

relatively inactive in the colloidal silver model systems. The less active compounds are probably poorly adsorbed to the silver particles as judged by the fact that relatively larger quantities are needed to cause a retardation of physical development.

Since the sensitivity centers may be partly composed of silver sulfide the behavior of a silver sulfide system was briefly examined. Finely dispersed silver sulfide catalyzes physical development and 5-phenyl-1-mercaptotetrazole retards the catalytic activity in much the same manner as with the colloidal silver system.

The similarity of effects of these stabilizer compounds in the photographic emulsion and the colloidal silver model systems suggests a common mechanism. Although silver salt formation on the surface of the silver halide crystal is not precluded, adsorption on a silver sensitivity speck is sufficient to account for the retardation of chemical sensitization observed with certain compounds. This view is in accord with that of Koseki and explains why quantities much less than that required for a monomolecular layer on the entire silver halide crystal are needed. Retardation of chemical sensitization is due to the suppression of the catalytic activity of silver particles which thus prevents their growth into an effective sensitivity speck.

The catalytic activity of the silver development centers for development is reduced. Thus, a reduction in emulsion speed results when a compound such as the mercaptotetrazole is added to the sensitized emulsion prior to coating. A practical stabilizer is one which can be added after the second digestion and which prevents any further silver speck growth during storage, but which at the same time is not so strongly adsorbed as to interfere with subsequent development.

Conclusions

Organic stabilizers were observed to retard the rate of sensitization during the second digestion of a medium speed photographic emulsion. Effective compounds were shown to reduce or eliminate the catalytic activity of colloidal silver in physical development. A mechanism of sensitization retardation is proposed in which organic stabilizers adsorb to the surface of active sites or partially formed silver sensitivity centers and render the centers catalytically ineffective. Successful stabilization of aging fog must involve the introduction of stabilizing compounds after emulsion sensitization is complete and such compounds must be easily desorbed during development in order not to interfere with development rate and film speed.

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Melting Point of Gelatin Gel Containing Chrome Alum as a Hardening Reagent

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The melting point of gelatin gels containing chrome alum is measured under various conditions of gelatin concentration, chrome alum content, and reaction time. The hysteretic effect of the system after addition of chrome alum is also investigated in some detail.

Marked elevation of the melting point is observed for gels obtained by cooling soon after the addition of chrome alum, but not for gels obtained by cooling at a time long after the addition. The melting point of the latter is often depressed below that of the no-chrome-alum gel. This shows that the chromium links formed in the gel state can promote the hardening effect, but the chromium links formed in the sol state rather counteract the hardening effect.

For interpreting these phenomena, it is suggested that in the gel state chromium links are formed in the amorphous region of the gel structure and make the gelatin micelles more stable for heating, while chromium links formed in the sol state rather interfere with the development of gelatin micelles and make the melting point of the gel lower than that of non-treated gels.

In this paper, we try to make some contributions to the interpretation of the hardening effect of chrome alum on gelatin by measuring the melting point of the hardened gels under various conditions.

In the absence of chrome alum, gelatin sols gel when cooled below a definite temperature. As is well known, this transition from sol to gel is, at least in an approximate sense, a thermodynamic one primarily related to the formation of microcrystals (often called *micelles*) of gelatin molecules.[1] Thus we may conveniently refer to gels of this kind as *reversible* gels.

On the other hand, the chromium complexes link together two adjacent polypeptide chains by attaching with covalent forces to the acid groups of one chain and with coordination valencies to the basic groups of the other chain.[2] The presence of linkages of this kind itself presents the possibility of forming an infinite network of the molecular chains. Thus, the gelatin sol often is transformed to gel without cooling if a large amount of chrome alum is added. As the reaction of chrome alum with gelatin is of irreversible nature and gels thus obtained are difficult to resolve, we may conveniently refer to gels of this kind as *permanent* gels.

The third type of gelatin gel is the *hardened* gel which is obtained by cooling the sol containing a relatively small amount of chrome alum. In these gels, there exist both the linkages of chrome alum and the microcrystals of gelatin molecules. Therefore the behavior of such hardened gels should be interpreted in terms of the cooperation between the formation of the chromium linkages and the crystallization of gelatin. Here we present the results of our investigation of the properties of hardened gels.

The behavior of gelatin gels containing chrome alum is of much interest in connection with the hardening of photographic emulsions or the tanning of collagen. Therefore research on the cooperation mentioned above should provide some valuable information for the photographic and the tanning industries.

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Experimental Procedures

The gelatin sample used in this study was BN 29–1, from the Nippon Leather Co., obtained from limed calf skin. Its intrinsic viscosity was 0.331 dl/gram at the isoelectric pH of 4.8 in 0.05 molar potassium chloride solution at 40°C. The gelatin solution was prepared by dissolving at 43°C after swelling at room temperature. This method of preparing the gelatin sol is satisfactory to assure a solution free from hysteresis. The pH of the sol was adjusted to 5 by NaOH and HCl as soon as possible after the addition of chrome alum.

The melting point of the gel was measured by the falling ball method. Seventeen milliliters of the gelatin solution were poured into a 20-mm-diameter test tube and gelled at 0°C; then a small glass ball was placed in the gel at 1.5 cm from the surface. The test tube was kept at 4°C in a well-stirred water bath for a definite time for aging; then the bath was warmed at the rate of 0.2°C/min. The temperature at which the ball fell to the bottom of the tube was read as the

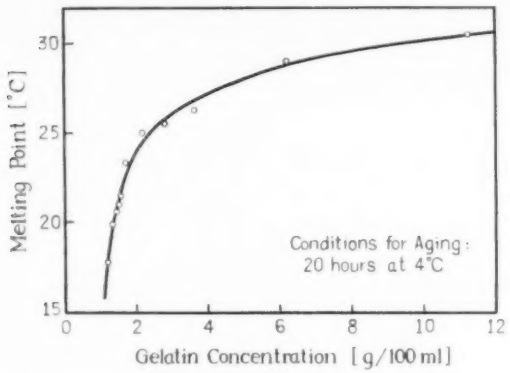

Fig. 1. Melting point of gelatin gels as a function of concentration.

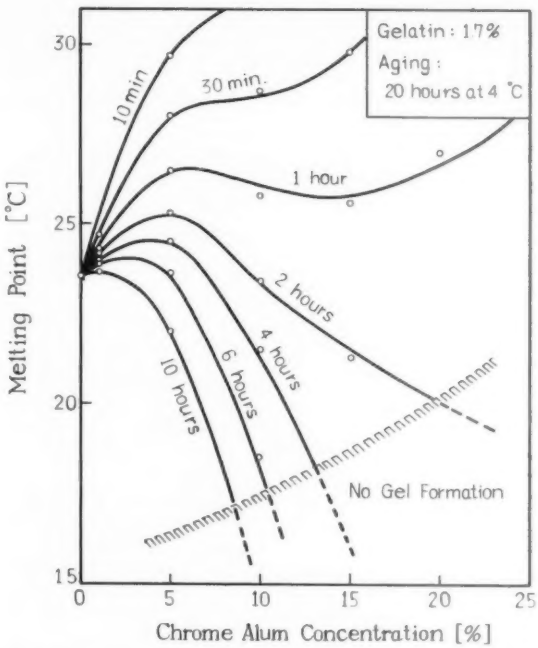

Fig. 2. Variation of melting point when chrome alum is added in various amounts. Reaction time is indicated on each curve.

melting point. The reproducibility of the melting point data obtained by this method was within 0.5°C.

The melting point of gels containing no chrome alum increases with the concentration of gelatin, tending towards a limiting value, and increases slightly with aging time also. At concentrations lower than about 1 gram/100 ml, however, sols cannot undergo gelation even if cooled in ice water for long periods of time. Figure 1 shows the relation between the gelatin concentration and the melting point of gel, and the chain curve in Fig. 4 illustrates the influence of the aging time on the melting point of 1.7% gel. Here the term 1.7% refers to the gelatin concentration of 1.7 grams/100 ml.

The effect of chrome alum on the melting point of the gel was first studied using 1.7% gel as an example. After the addition of an amount of chrome alum, the gelatin sol was kept at 43°C for a definite period of time to enable the chrome alum to react with the gelatin molecules in the sol state. Then the test tube containing the sol was plunged into ice water for gelation, and after aging for a definite period of time at 4°C, the melting point was measured. For the sake of convenience, we refer to the time elapsed between the addition of chrome alum and cooling as the "reaction time," and the time elapsed after cooling as the "aging time." The melting point data thus obtained are of course much dependent on the amount of chrome alum and on both the reaction and the aging times.

The effect of the chrome alum concentration on the melting point of the 1.7% gel is shown in Fig. 2, together with the effect of reaction time. The amount of chrome alum is expressed in terms of its weight percentage to the gelatin weight and the aging time is here kept constant at 20 hr. The melting point is appreciably diminished with the increasing reaction time, and if the reaction time is prolonged too far beyond a limit, the sols become unable to form the gels. Such a limit for the reaction time is about 6 hr for 10% addition of the chrome alum and 2 hr for 20% addition. On the other hand, when the sol is cooled soon after addition of the chrome alum, the melting point is always markedly raised and often reaches a very high value.

In Fig. 3, the melting point data from Fig. 2 are replotted against the reaction time for clearer understanding of the foregoing statements; and in Fig. 4, the influence of aging time is illustrated. From these figures we may conclude that the reaction which proceeds between gelatin *gel* and chrome alum makes a positive contribution to the elevation of the melting

TABLE I

Method of Preparation of Three Kinds of Gels with Different Histories

43°C sol (1.7% gelatin)	→ 43°C Sol	→ Sol A	→ Gel A
		Adding chrome alum and keeping at 43°C for 3 or 5 hr	Cooling and aging at 4°C for 3 days
	→ 30°C Sol	→ Sol B	→ Gel B
Cooling from 43° to 30°C		Adding chrome alum and keeping at 30°C for 3 or 5 hr	Cooling and aging at 4°C for 3 days
→ 0°C Gel →	30°C Sol	→ Sol C	→ Gel C
Cooling	Heating for melt	Adding chrome alum and keeping at 30°C for 3 or 5 hr	Cooling and aging at 4°C for 3 days

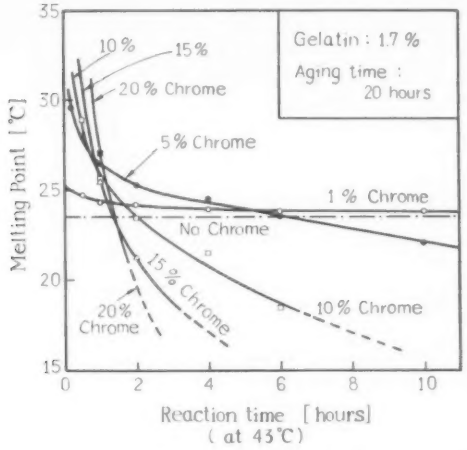

Fig. 3. Variation of melting point as a function of reaction time at 43°C. Chrome alum concentrations are indicated on each curve.

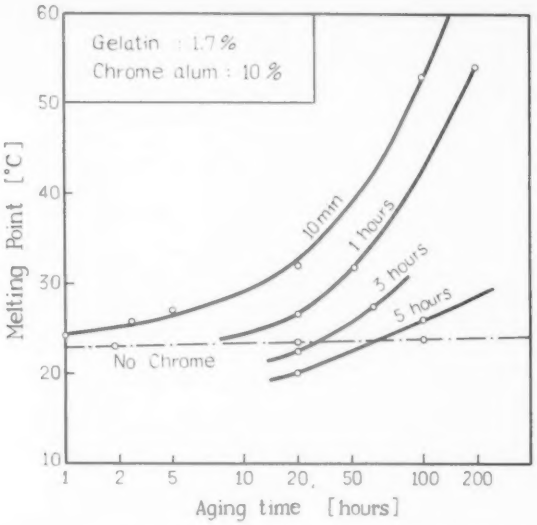

Fig. 4. Variation of melting point as a function of aging time at 4°C. Reaction times at 43°C are indicated on each curve.

point of gels, while the reaction proceeding between gelatin *sol* and chrome alum does not.

This conclusion is also supported by the following experiments. We prepared three types of gel — A, B, C — with the same composition but with different histories, following the procedures schematically shown in Table I. Their melting points were measured and the results are given in Table II. As has already been shown by various investigators,[3] at temperatures lower than about 40°C, gelatin molecules in the sol are more or less in aggregation due to the existence of crystallite residues, and the degree of aggregation is appreciably influenced by the history of each sol. In our three samples, as might be expected, the degree of aggregation was ordered as C > B > A. The fact that this order is the same as that of the melting points in Table II seems to prove, consistent with the foregoing conclusion, that the hardening effect of gel results mainly from the reaction of the chrome alum with the gelatin molecules in aggregation. The gel state is nothing but an aggregated state with a macroscopic dimension.

The effect of repetition of the sol-gel transition was also studied. After a gel containing chrome alum was melted and heated up to 43°C to resolve the residues of microcrystals, the sol was again cooled in ice water to obtain regelled samples. Table III shows the melting point of the regelled gels thus obtained. In the absence of chrome alum, such repetition of the sol-gel transition does not have any influence on the melting point, but in the presence of chrome alum, the melting point of the regelled gel was markedly lower than that of the primary gel. An interpretation of this observation is given in the following section.

Finally, we carried out experiments similar to those described above, but using gelatin concentrations other than 1.7%. Gels of 2.2%, 2.8%, and 3.6% were tested, with aging time fixed at 20 hr at 4°C but both the reaction time and the chrome alum content being varied. Figures 5 and 6 show the results; in Fig. 5 the reaction time is 1 hr and in Fig. 6 it is 6 hr. The melting point data for the gels containing 5%, 10%, and 20% chrome alum are plotted against the gelatin concentration.

Figures 7 and 8 give the melting points of hardened gels as functions of gelatin and chrome alum concentrations. These figures are obtained from the data in Figs. 5 and 6. Some noticeable variations with the reaction time are observed in the shape of the contour of the melting point curves. First, the no-gel region, where the sols cannot form gel (even by the 20-hr aging at 4°C), extends towards the high concentration

TABLE II

Melting Point of Three Different Types of 1.7% Gelatin Gels Involving 10% Chrome Alum

Gel type	Reaction time, hr	Melting point, °C
A	3	32.0
	5	25.8
B	3	51.0
	5	37.8
C	3	65.0
	5	56.0

TABLE III

Melting Point of Regelled Gels

Concentrations		Reaction time at 43°C	Aging time at 4°C	Melting point, °C	
Gelatin	Chrome alum			Primary gel	Secondary gel
1.7%	0%		1 day	27.2	27.0
1.7%	10%	10 min	1 day	35.0	24.5

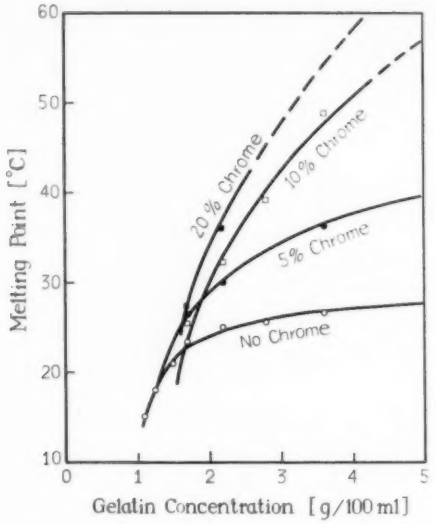

Fig. 5. Melting point of gel as a function of gelatin and chrome alum concentrations — I: reaction time, 1 hr at 43°C; aging time, 20 hr at 4°C.

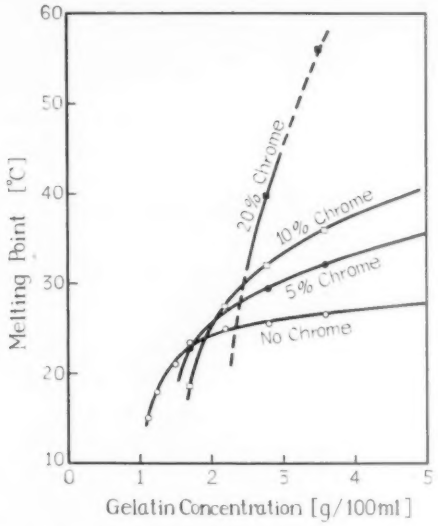

Fig. 6. Melting point of gel as a function of gelatin and chrome alum concentrations — II: reaction time, 6 hr at 43°C; aging time, 20 hr at 4°C.

side of gelatin if the reaction time is increased. Secondly, the permanent-gel region where the sols turn into gel without cooling is also enlarged with the reaction time and, at high concentrations of chrome alum, after the 6-hr reaction time, this region nearly makes contact with the no-gel region. Thus we may suggest that, when a large amount of chrome alum is added, the no-gel and the permanent-gel regions are separated from each other by a critical condition for the gelatin concentration. As shown in the following section, the existence of this kind of critical separation is closely related to the counteraction between the inter- and the intramolecular linkage which was first suggested by Pouradier.[4] Between the no-gel and the permanent-gel regions lies the hardened-gel region, in which the sol-gel transition shows a typical irreversible nature, i.e. the setting point is lower than 43°C but the melting point often becomes higher than 43°C. This undoubtedly arises from the reaction between chrome alum and gelatin which proceeds after gelation.

Discussion

As was emphasized by Pouradier,[4] the chromium linkage is formed between acid and basic groups of the same chain as well as of adjacent chains. Thus the addition of chrome alum always introduces both inter-

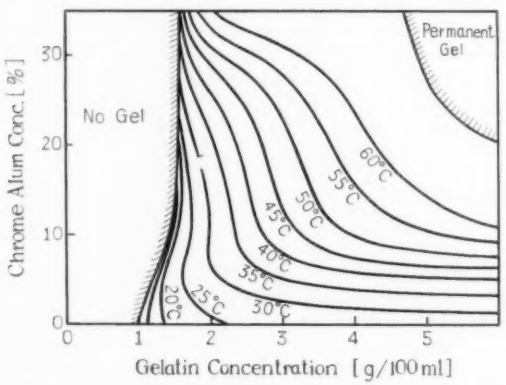

Fig. 7. Melting point of hardened gel as a function of gelatin and chrome alum concentrations — I: reaction time, 1 hr at 43°C; aging time, 20 hr at 4°C.

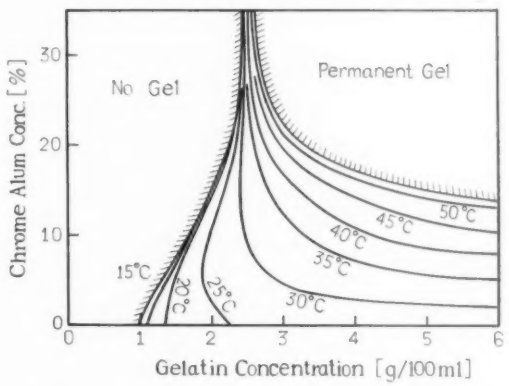

Fig. 8. Melting point of hardened gel as a function of gelatin and chrome alum concentrations — II: reaction time, 6 hr at 43°C; aging time, 20 hr at 4°C.

and intramolecular linkages into the system, though the relative proportions of the two kinds of linkages must depend on the gelatin concentration and other experimental conditions. The formation of the intramolecular linkages cannot contribute to the gel formation, but does contribute to the diminution in the statistical radius of molecular coil or to the increase of the intermolecular distance. Hence, the formation of the intramolecular linkage would accelerate further formation of the same kind of linkage and counteract formation of another kind of linkage — the intermolecular linkage — at any instant which follows. In addition, it is also to be noted that the multiple formation of the linkages between two molecules diminishes the radius of the aggregate which is formed by the first linkage. It appears, therefore, that if the intramolecular link formation dominates the intermolecular one at the first stage of the reaction, the domination of the former becomes more decisive with the proceeding reaction at the following stage. This kind of autocatalytic nature of the reaction seems to offer an explanation for the tendency, shown in Figs. 7 and 8, of the no-gel region to extend toward the high concentration side of gelatin with increasing reaction time.

The critical concentration which separates the no-gel region from the permanent-gel region would correspond to the concentration at which the type of dominant linkage formed at the first stage of the reaction changes from the intramolecular one to the intermolecular one. Figure 8 shows that this critical concentration is about 2.6 grams/100 ml of gelatin.

In the absence of chrome alum there is also a critical value of the gelatin concentration near 1 gram/100 ml which separates the reversible-gel region from the no-gel region. The consideration about the chromium linkage mentioned above may be applicable to this case too, in which the microcrystals of gelatin molecules offer the linkages of gel structure taking the place of the chromium linkage. There is, however, an important difference between the two linkages — the chromium linkage and the microcrystal of gelatin. That is, the former is rather easily formed in the intramolecular manner, while the latter forms with difficulty. Thus the linkage of the microcrystal would almost always be of the intermolecular nature which contributes effectively to the gel formation. The situation noted here naturally explains the observed difference between the two critical concentrations, 1 and 2.6 grams/100 ml, corresponding to the no-gel–to–reversible-gel and the no-gel–to–permanent-gel transitions, respectively.

The curve line separating the hardened-gel from the no-gel region may be interpreted as a mixture of the two extremes, the one controlled by the chromium linkage alone and the other controlled by the microcrystal linkage alone.

Recently, Pouradier reported that the viscosity of gelatin solutions is diminished by the addition of chrome alum at concentrations lower than about 0.85 grams/100 ml of gelatin, and explained this diminution in terms of the formation of the intramolecular linkage. This phenomenon is, of course, very closely related to the critical separation between the no-gel and the permanent-gel regions explained above, although the gelatin concentrations characteristic of these two phenomena — 0.85 and 2.6 grams/100 ml — do not coincide with each other. Concerning this difference, we note that the solution viscosity is markedly influenced by the formation of aggregates but relatively less so by the shrinkage of the gelatin coil. Therefore, it appears reasonable that the critical concentration shifts towards a lower value in the case of the viscosity than in the case of the gel formation.

Now we turn to discussion of the melting point of the hardened gel. As is easily seen, the formation of microcrystals requires a relatively large rearrangement of chain configuration of the gelatin molecules. It is also natural to consider that the rearrangement of the gelatin chains, and accordingly the formation of the chromium linkage, appreciably interferes with the development of the microcrystals. Furthermore the melting point of the hardened gel would be primarily determined by the ease of resolving of the microcrystals. These considerations explain the behavior of the melting point of the hardened gels which decreases with increasing reaction time and chrome alum content as was illustrated in Fig. 3. The simple assumption that there must be a parallelism between the increase in solution viscosity and in melting point of the corresponding gel is thus rejected.

On the other hand, if the sol is cooled soon after the addition of chrome alum, a large part of the reaction between the chrome alum and the gelatin would proceed slowly in the gel state. In this case, the chromium linkage would form mainly in the amorphous region of the gel structure but not in the microcrystals. Since the thermodynamic stability of the

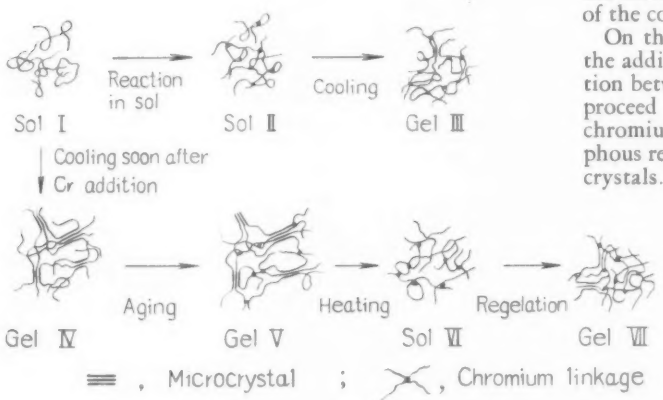

Fig. 9. Schematic illustration of network formation by the chromium linkages and the microcrystals.

microcrystal depends on the activity of the thermal (or Brownian) movements of chain segments in amorphous parts, such link formation in the amorphous region must make the microcrystals more stable against thermal disruption. The conspicuous rise in the melting point observed in the gels corresponding to a short reaction time seems to be caused by this effect.

These situations are schematically represented in Fig. 9. When the formation of the chromium linkages proceeds mainly in the sol state, we arrive at Gel III after cooling, having passed through a Sol State II with high viscosity. The melting point of Gel III is expected to be relatively low, compared to that of Gel IV, because of the underdevelopment of microcrystals. On the other hand, if Sol I is cooled soon after the addition of chrome alum, we arrive at Gel V after a long time for aging. The melting point of this kind of gel is generally expected to be higher than that of Gel IV. Now, if Gel V is melted by sufficient heating, Sol State VI, essentially similar to Sol II, is obtained. Therefore, Gel VII, obtained by the regelation of Sol VI, cannot show again as high a melting point as Gel V did, but behaves like Gel III. The results shown in Table III can be explained by this means.

Comparison of the melting points of three gels in Table II gives another proof of the foregoing consideration. That is, as easily seen, the number of residues or nuclei of the microcrystals is largest in Sol C and almost zero in Sol A, which is kept at 43°C. Thus among the three gels, Gel C, which bears the closest resemblance to State V in Fig. 9, naturally shows the highest melting point, and Gel A, corresponding to State III, the lowest one.

It should not be overlooked that the link formation is not a unique action of the chrome alum on gelatin. As was pointed out by Gustavson,[2] it is also possible for the chrome alum to react with gelatin on the $-COO^-$ groups. Such a unipoint binding would also interfere with the development of microcrystals as the chromium linkage does, though the effect would be comparatively weak.

In any event, in order to harden the gelatin gel effectively, it is not advantageous to keep the sol at high temperature after the addition of chrome alum.

Summary

The melting point of gelatin gels containing chrome alum has been measured under various conditions. It has been observed that the melting point of gel does not simply increase with reaction time and chrome alum content, and that the reaction of chrome alum with gelatin *gel*, but not with gelatin *sol*, contributes mainly to the hardening of the gel. Illustrations have been given to make clear the relationship of the melting point, the gelatin concentration, and the chrome alum concentration to one another. The mechanism of cooperation between the crystallization of gelatin and the chromium link formation has been discussed in some detail.

Acknowledgments

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The Quality of Water for Photographic Processing

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There are no standards for the purity of water required for processing photographic materials. This paper describes the photographic effects of impurities sometimes found in water. The effects of water hardness, suspended matter, chlorine, chloride, algae, slimes, pH, copper, iron, manganese, lead, fluoride, zinc, tin, total salt content, and sulfide are described.

The quality of the water available for photographic processing is important because of the effects that even small quantities of impurities may have on the processing. This is true partly because of the nature of the photographic process and partly because the quantity of water used far exceeds the combined quantities of all other chemicals. For example, a continuous processing machine for Eastman Color Films consumes approximately 1400 gph. A large processing laboratory may use as much as 100,000 gal of water per day. Of course, the quantity of water used by a laboratory may depend on its scarcity or cost.

Standards have not been formulated for the quality of water because some photographic processes require "purer" water than others and because the success or failure of water of a given quality may depend as much on how the water is used as upon its chemical composition. Flow rate, temperature, and type of agitation may affect the suitability of a particular water for a particular process.

Although there are no standards for water, some information about the photographic effects of impurities in water may be helpful in deciding the location of a new plant or in diagnosing a processing difficulty in which the water is questioned. Because of the varied sources of waters, it is understandable that their compositions vary tremendously. Fortunately, most municipal water supplies are of adequate purity for most photographic processes. First thoughts might suggest distilled water as a standard. However, distilled water may cause emulsion reticulation or softening. On the other hand, dissolved salts which may prevent reticulation may cause some unwanted photographic effect.

The variety of impurities in water supplies is almost unlimited and only the more common ones are reported here. It should be kept in mind that the only conclusive test of the suitability of a water is a production trial. The laboratory test results reported here may serve as a valuable guide, but the information is not submitted as a standard for the quality of water for processing.

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Water Sources and General Composition

Water is obtained from either surface or underground supplies. Generally, the chief difference between these two sources is hardness. Surface waters, such as rivers and lakes, average approximately 100 parts per million (ppm) hardness, while underground waters average 200 ppm hardness; however, there is a wide range of hardness within each type.

Either quantity or quality of water may be a controlling factor in the location or proper operation of a photographic processing laboratory. There is little leeway in the amount of water that is to be used for the processing solutions for a given process, but wash-water flow rates allow for large differences in amounts of water consumed. An increase in wash rate in a wash tank following a processing solution minimizes the possibility of contamination in that wash. A decrease in flow rate increases the danger of higher contamination that may cause adverse photographic effects. Low wash rates in the final wash of a process may leave hypo in the product, which can lead to the more rapid fading of dyes in color products, especially cyan dyes.

Constancy in composition of a water supply is an obvious advantage, although some changes in chemical composition may be well within the photographic tolerances. Seasonal changes in river waters are common. Municipal treatment of water may change seasonally or because of changes in sources of supply. The local weather may influence a water supply. For example, the Chicago water supply from Lake Michigan may be much more turbid and higher in silica when there is a strong wind from an easterly direction.

Some municipalities have several sources of water which are very different in composition. A customer may be supplied primarily from one source, and, without notice, the supply may be fed from another source, with a different type of water. The municipal supplies in Los Angeles and Dallas have been known to change abruptly. In the Los Angeles area, water is supplied from sources that differ tremendously in composition. Some average analyses are shown in Table I.

TABLE I

Chemical Analyses of Los Angeles Water

Averages for Fiscal Year 1954-1955

	Owens Valley Aqueduct Sources	Los Angeles River Conduit	Metropolitan Water District
Dissolved solids	218 ppm	389 ppm	700 ppm
Total hardness, as $CaCO_3$	89 "	209 "	127 "
Sulfate (SO_4)	23 "	107 "	294 "
Chloride	19 "	39 "	86 "
Calcium	26 "	60 "	32 "
Magnesium	6 "	15 "	12 "
pH	8.4	7.8	8.4

Hardness

The hardness of water is essentially a measure of the calcium and magnesium ions that are present. Hardness is generally expressed as calcium carbonate. Water is considered hard if by analysis it is found to contain more than 100 ppm* (expressed as calcium carbonate). The American Standards Association now has in committee a proposed standard for the determination of water hardness. However, it is not planned that this standard will cover limits of hardness for photographic processing.

Processors who use municipal water supplies generally can obtain water-hardness analyses, as well as other chemical analyses, from their municipal water offices. The municipality usually can also furnish information regarding seasonal or other fluctuations in chemical composition of the supplies. This information may be more reliable than an isolated chemical analysis.

Water conditioning service is available in many localities. Organizations offering such service are usually well informed regarding the quality of the existing water supplies and how these waters may be treated to accomplish specific objectives. However, the most frequent conditioning service is water softening, for iron removal, or for making water safe for drinking purposes. These factors may be or may not be important to the photographic processor.

Calcium and magnesium, when present in sufficiently high concentrations, may be precipitated in the processing solutions as carbonates, sulfites, phosphates, or borates. This behavior is, in part, a function of the pH of a processing solution; the tendency toward precipitation of calcium carbonate or calcium sulfite is increased as the alkalinity of a processing solution increases. Calcium does not precipitate in acid processing solutions.

Calcium and magnesium also build up scale in heat exchangers, water lines, processing tanks, etc.; in extreme cases, the precipitate may deposit onto the film or paper during processing. A Hollywood processing laboratory found a correlation between hardness of water, used at different seasons of the year, and the number of scratches found on processed film. The correlation is shown in Fig. 1.

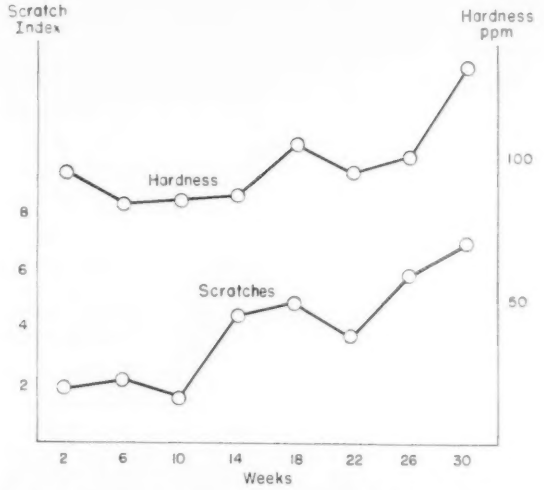

Fig. 1. Correlation of hardness of water used and scratches found on processed film by a Hollywood processing laboratory.

Precipitation due to hardness may be minimized or avoided by the addition of a sequestering agent such as Calgon* or Quadrafos.† A concentration of 0.5 grams/liter is a practical amount for water containing 100 ppm hardness. Some photographic processes, however, are adversely affected by certain sequestering agents.

A metaphosphate sequestering agent in a processing solution will slowly hydrolyze to orthophosphate and may finally precipitate as calcium phosphate, which may be mixed with calcium carbonate. The precipitate may adhere to equipment or to the product. Without the sequestering agent the calcium carbonate precipitate might be even more troublesome.

Chelating agents such as ethylenediaminetetraacetic acid (EDTA) have been used successfully in some cases to minimize or prevent precipitation due to hardness, but EDTA cannot be used in some solutions because it causes more rapid loss of certain developer constituents such as hydroquinone. Thus such an additive should be checked for possible photographic effects.

Mader[1] recently reported that EDTA added to a developing solution exposed to air forms a ferric iron complex if there are traces of iron present. The complex catalyzes a reaction of the developing agent. In the absence of EDTA, there is little loss of developing agent.

Very hard water is sometimes used in spite of the more turbid mixes and washes it produces. Some

*An older custom has been to report all constituents in units of grains per gallon. Grains per gallon may be converted to parts per million by multiplying by 17.1.

*Calgon, Inc., 220 Delaware Ave., Buffalo 2, N.Y.

†Rumford Chemical Works, 31 Newman Ave., Rumford 16, R.I.

processors filter their mixes; others allow them to stand until the precipitate settles. Economic factors may determine the practice followed.

In most hard waters in the usual pH range of 6 to 9, the bicarbonate/carbonate ratio is high — i.e., the water contains a high concentration of bicarbonate and very little carbonate. Bicarbonate furnishes some buffering of the water at a pH near 8. Cases where bicarbonate or carbonate ions have an adverse photographic effect are rare. However, in the prehardener of the Kodachrome K-11 process, the presence of a few hundred ppm of bicarbonate is objectionable because it produces a low blue density. In a processing laboratory in Dallas, Texas, bicarbonate is removed by acidifying the water and bubbling air through it to liberate the carbon dioxide.

Excessive hardness in the water used for the color developer of the Kodacolor Film C-22 process produces lower contrast, especially in the yellow and cyan dyes. The C-22 process is balanced for water of average hardness and thus no difficulties should be expected with most water supplies, but, if hardness is excessive, unwanted photographic effects can be avoided by reducing the hardness with ion-exchange equipment. The ion-exchange process substitutes sodium for the calcium and magnesium, while the bicarbonate content is not altered.

The use of soft water is not without its problems with certain films. Soft water may allow an emulsion to soften to such an extent that it is easily scratched or reticulated, or even removed from the base during processing. The addition of 1 gram of magnesium sulfate per liter to the appropriate processing solution or wash water has been found to prevent the softening problem in certain instances.

Suspended Matter

Water may be turbid because of silica, dirt, or other materials carried from the source. Turbid solutions are objectionable because of the settling out of the suspended materials on the equipment or the product. Dirt may also cause scratches on the emulsion. Some processing laboratories in the Chicago area employ filters to prevent intermittent troubles from turbid water.

Chloride

Most municipal water supplies contain less than 25 ppm of chloride ion, an amount to which most processes are insensitive, although in a reversal black-and-white process, a chloride concentration of 25 ppm in the bleach may cause some re-reversal of the image. At higher concentrations, chloride has a restraining action on development. When chloride is the only objectionable constituent in the water, it is practical to pretreat the water with an equivalent amount of silver nitrate and to allow the silver chloride to precipitate. The silver can be recovered. Only for those processing solutions sensitive to chloride need water be treated for chloride removal.

Sea water or underground briny waters have an intolerable level of chloride for most processing purposes. Chloride also adds to the corrosive action of water on the processing equipment. In special cases, however, such water can be used in washing operations[2,3] (see end of section on *Wash Water*, below).

Chlorine

The chlorine content of most drinking water is low enough to be safe for processing. In processing solutions containing sulfite, there will never be any free chlorine because of its reduction by the sulfite. Some films, however, are especially sensitive to chlorine prior to the time they reach the first developer. In such cases, a prebath containing only sulfite may be used to eliminate the free chlorine in the water.

Algae and Slimes

Organic material such as algae, molds, diatoms, and bacteria may appear in water supplies in varying amounts, depending on the water source, the season, the weather, or other factors. Both living and dead diatoms have appeared in water supplies in the Hollywood area. Water companies can prevent such growths or kill the organisms by treatment with chlorine, sodium hypochlorite, or a bactericide such as Dowicide G. Some processors have found it necessary to take further precautions by filtering their water or using additional chlorine.

pH

Most water has a pH value between 6 and 8. Few waters have enough dissolved salts to buffer the water sufficiently to produce any effect on the pH of a processing solution, although water from a deep well in the Dallas area does have such an effect. The less buffering agent there is in the processing solution the greater will be the deviation of the pH from standard. The major constituents of the Dallas water are shown in Table II. The most unusual characteristics of this water are its high content of sodium bicarbonate and sodium sulfate in relation to its low hardness. The bicarbonate content buffers the water at pH 8.2, so that certain processing solutions prepared with it

TABLE II
City of Dallas Well Water — Well No. 39

	ppm
Dissolved solids	1040
Sodium	385
Bicarbonate	542
Sulfate	259
Chloride	95
Calcium	6
Magnesium	2
Silica	22
Hardness, as $CaCO_3$	24
pH	8.2

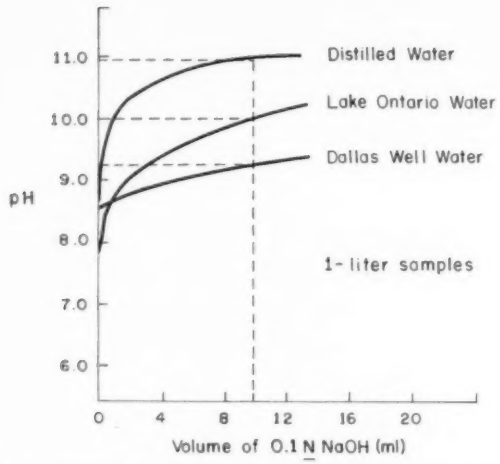

Fig. 2. Comparisons of buffering capacities of different types of water.

require an additional amount of sodium hydroxide to bring the pH of the final mix to standard. The buffering capacity of this water is shown by a curve in Fig. 2, where it is compared with Lake Ontario water and distilled water.

Copper

Excessive amounts of copper cause emulsions to fog and cause loss of developing agents. Fortunately, few supplies contain more than a few hundredths ppm. Although some water lines are made of copper, the water in the lines does not dissolve appreciable amounts of copper.

Municipalities occasionally add copper sulfate to water to kill algae in reservoirs and mains. This treatment is often done intermittently rather than continuously and thus it is difficult for the processor to determine whether abnormal results might be due to copper.

One ppm copper causes significant loss of a color developer after two weeks (see Fig. 3). Ten ppm cause appreciable loss within a few days. Photographically, 1 ppm copper is tolerable though visible in Ektacolor Paper, Type 1384, but 10 ppm produce serious fog.

Sulfide

Sulfide causes photographic fog. One ppm sulfide is acceptable in Ektacolor Paper, Type 1384, but 10 ppm fog the paper almost completely. Kodachrome Film has a similar sensitivity to sulfide.

Sulfides are rarely found in surface waters because they are generally lost at the surface as hydrogen sulfide. Well waters sometimes contain sulfides which can be detected by the odor of hydrogen sulfide. Fortunately, the odor test is so sensitive that if hydrogen sulfide is not noticeable by odor its concentration is probably too small to cause photographic

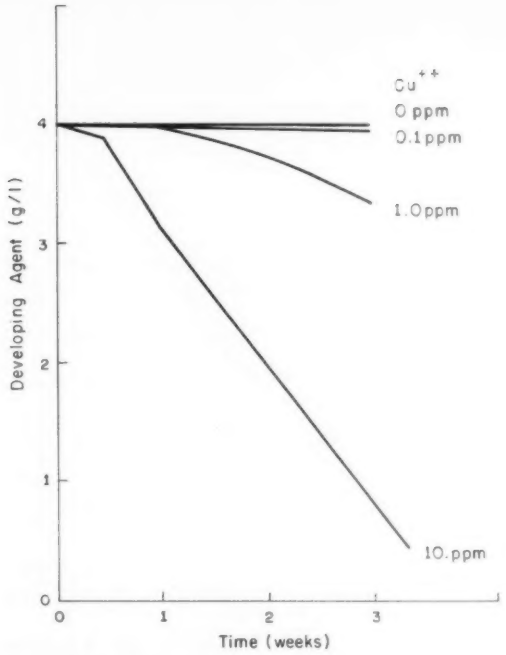

Fig. 3. Effect of copper in causing loss of developing agent in a color developer.

difficulties. Amounts as low as 0.1 ppm can be detected by odor.

It cannot be assumed that all types of film and paper are of equal sensitivity to fogging by sulfide or, for that matter, by any other contaminant.

Iron and Manganese

Iron frequently occurs in ground waters to the extent of several tenths ppm or more. Surface waters rarely contain over a few ppm of iron. Greater than 0.1 ppm of iron may cause trouble, with staining of the product, but some products will tolerate as much as 10 ppm ferrous or ferric iron. Such is the case for Ektacolor Paper, Type 1384, according to laboratory tests. However, iron in concentrations above 0.1 ppm may cause trouble, over a period of time, by depositing as rust in the tanks or on the product.

Ground waters that are yellow in color may contain iron or organic matter. The iron will be primarily ferrous iron because of the absence of oxygen, but when ground water is exposed to air, the ferrous iron oxidizes to ferric iron. After short periods of standing the water may become more yellow or red due to this oxidation. After extended standing, the ferric iron gradually precipitates as ferric oxide rust, thus resulting in water that is less yellow in color. In fact, one of the conventional commercial techniques is to aerate water and allow it to stand in the reservoir until the ferric iron precipitates. Alternatively, water-conditioning equipment, such as an ion-

exchange column, is available for removing iron as well as calcium and magnesium.

Manganese is probably more harmful than iron in its staining propensity, but fortunately few waters contain enough manganese to be troublesome.

Tin, Lead, and Zinc

Up to 10 ppm tin, lead, and zinc ions may be present without producing adverse photographic effects on Ektacolor Paper, Type 1384, by laboratory tests. At concentrations up to 10 ppm these ions had no accelerating effect on decomposition of developing solutions kept standing for periods up to 3 weeks. Fortunately, waters usually contain negligible concentrations of these ions.

Lead-tin solder should be avoided in processing equipment because it is a potential source of contamination, which may be objectionable photographically or chemically on certain products.

Fluoride

Fluoride, in concentrations up to 1 ppm, is added to many water supplies. Laboratory tests on several color products indicate no photographic effect from fluoride up to at least 10 ppm.

Wash Water

The formation of a calcium precipitate in a wash water may be due to hardness or to calcium leached out of the film. If the preceding processing solution contains carbonate, borate, or phosphate, the salt will be carried over to the wash water and will cause the precipitation of the calcium.

Drying spots may occur on film because of water remaining on the film just prior to the drying stage. This problem is more serious if there is a high salt content such as in hard water. The drying spots may be minimized or avoided by the use of an air squeegee or by addition of a suitable wetting agent to the final wash.

The use of sea water or other water of high salt content for washing purposes has been described by Eaton and Crabtree[2] and by Crabtree and Henn.[3] Although salt water washes hypo out of the product faster than does distilled water, it is necessary to have a short wash with water of a low salt content following the wash with water of high salt content.

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Multiflash Photography

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There are many good reasons why electronic flash lighting is especially useful for multiple exposure photography: The flash interval can be accurately controlled; the initiation time can be precise; the exposure time can be controlled; the exact quantity of light can be determined. In this paper, several typical electric circuits for flash lighting are discussed, with special emphasis on a combination operated up to a 100-kc rate. A 1-μsec flash duration with 1.5 wsec/flash is used.

One of the most fascinating kinds of photography is the so-called multiexposure or multiflash type, in which several photographs are superimposed on the same negative. The French physiologist E. J. Marey was a leader in the use of this technique and probably its originator. In his book *Movement*,[1] published in 1895, Marey presented the results of careful studies of the ways in which animals and people move. To produce a series of pictures on one film, Marey employed a black background and a rotating disc shutter with narrow slots in front of the lens.

Among the other pioneers[2,3] in the development of electrical spark source methods are Bull, Cranz and Schardin. For the most part, they used bullets as their subjects and developed silhouette photography through application of the spark source.

The modern electronic xenon flash tube produces light more efficiently than a spark and can easily be controlled to flash at a desired time. Its increased light output makes possible reflected light photography with practical-sized equipment, numerous applications of which are currently in vogue. Primarily, this type of photography is employed in obtaining and presenting information about moving objects as a function of time,[2,3] but use of the system for educational and advertising purposes is also becoming common. The combination of xenon flash systems and Scotchlite screens for back lighting offers great promise for large area silhouette studies, some examples of which are described and illustrated below.

This paper also discusses some of the technical problems that arise when the system is applied to reflected-light ballistic photography in which both the exposure time per flash and the interval between flashes must be short. Because of the deionization effects of gas in the flash tube, it is more difficult at high frequency to operate a high-powered lamp than a low-powered lamp.

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Multiflash Light Sources

Multiflash light sources can be classified according to the following three general types:

(1) Separate lamps, each regulated by a separate energy storage circuit. The intervals are selected and each lamp flashes once.

(2) A common flash lamp operated by a fast rechargeable circuit which includes a rapid deionization control tube, such as a hydrogen thyratron or a mercury-arc tube.

(3) A common flash lamp operated by a series of separate energy storage circuits with rapid deionization devices for switching each energy source.

The units described here are in the last two classifications.

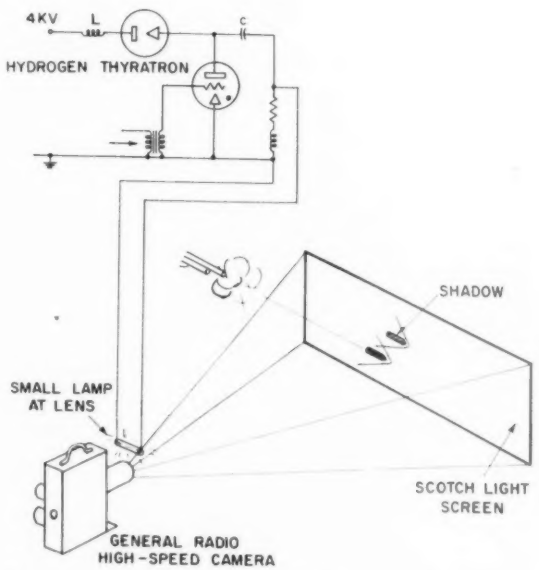

Fig. 1. Schematic diagram of a high-frequency stroboscope for bullet photography as used for the bullet photograph, Fig. 2.

Rapid Flashing Source

One high-frequency driving circuit[4] for an electronic flash lamp is shown in Fig. 1. In this circuit a hydrogen thyratron controls the starting and deionization of the flash tube. The deionization of the thyratron is such that capacitor C can be charged from the source so as to permit a 10,000 flash/sec rate. Because they are filled at high pressure with a rare gas which remains ionized long after each flash, the tubes themselves are notoriously long in their deionization process. However, the hydrogen thyratron with its rapid deionization time controls the stopping and restarting instants of the flashes.

Background lighting can be provided by the Scotchlite screen* indicated in Fig. 1. In this arrangement, the lamp has to be close to the lens for the Scotchlite to be most effective in reflecting the light. The shock wave can be photographed if the camera lens is focused on the screen and if a small light source is used to produce refraction effects.

Figure 2 shows a 30-caliber bullet leaving the muzzle of a gun. The photographic arrangement is similar to that shown in Fig. 1. The bullet velocity is about 2700 fps; the interval between exposures is 1/10,000 sec and the flash duration about 1 μsec. The camera used was a 35mm General Radio, Type 651AH. With 220 v, dc, on the motor, a film speed of about 120 fps was obtained. The camera, light, and gun were synchronized by the timer assembly of an EG&G High Speed Stroboscope, Type 501.

*No. 3270, silver, made by the Minnesota Mining and Manufacturing Co.

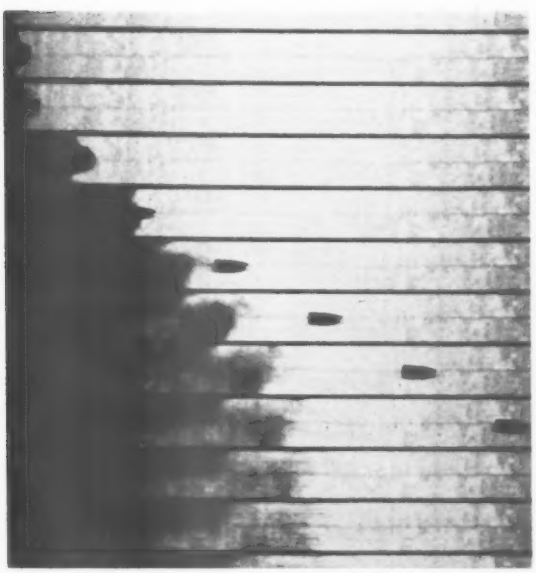

Fig. 2. A series of photographs taken at a 10-kc rate (100 μsec between exposures) on a continuously moving film (about 120 fps) in a General Radio Type 651AH camera. An FX-3 flash tube was used at the lens (2 in., f2) of the camera. The lamp was driven by an EG&G Type 501 High Speed Stroboscope, using a 0.01-mfd capacitor charged to about 8 kv. The camera lens was focused on the bullet.

Double-Flash Equipment

The double-flash unit,[5] EG&G Type 2307, was designed for silhouette photography of such subjects as dynamite caps, spray nozzles, paint guns, and bullets. The device is mounted in an expandable box; a plastic fresnel lens is placed on one end so the light output

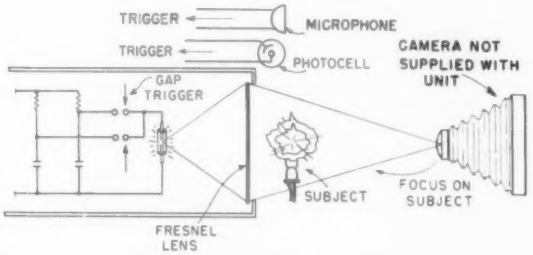

Fig. 3. Electrical and optical arrangement of the EG&G Type 2307 Double Flash Light Source.

can be efficiently used in a camera. The electrical and optical arrangements of the equipment are shown in Fig. 3. Figure 4 shows two shadow photographs of a 22-caliber bullet as it grazes off a string. The exposure is about $\frac{1}{5}$ μsec and the interval between exposures about 100 μsec.

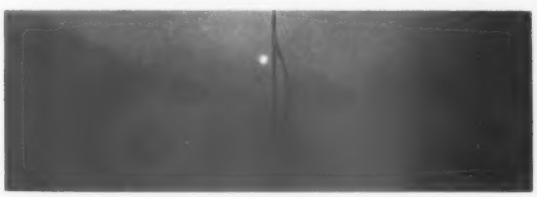

Fig. 4. Double-flash photograph of a 22-caliber bullet grazing a string. The interval between flashes is 100 μsec. The exposure time is about $\frac{1}{5}$ μsec.

The double-flash lamp has a $\frac{1}{8}$-in. air gap between 40-mil tungsten electrodes in a glass tube. The double flash is regulated by two trigger gaps, each of which controls the energy from a capacitor, as shown in Fig. 3. Since only two flashes are produced at each operation, there is no rapid recharge requirement for the capacitors, as there was in the High Speed Stroboscope, Type 501.

Multiflash Equipment

The first attempts to extend the circuits of the double flash to a 20-flash unit were limited in frequency by the deionization of the gaps. For reflected light photography at a 50-kc rate, the light requirement was 1.5 wsec/flash. Air gaps were sufficient to con-

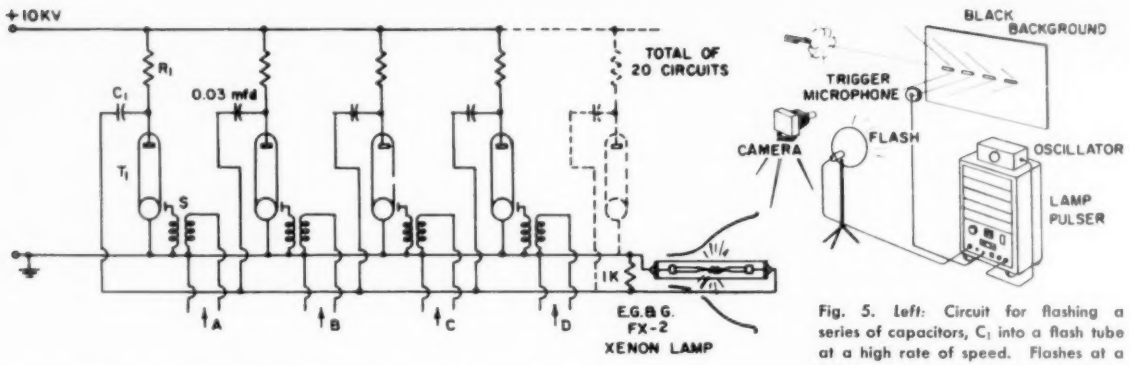

Fig. 5. *Left:* Circuit for flashing a series of capacitors, C_1 into a flash tube at a high rate of speed. Flashes at a 100-kc rate have been switched with 1.5 wsec/flash. *Right:* Setup for bullet photography.

trol the starting of the discharge, but the gaps would not deionize after each firing, and their conduction caused circuit difficulties in subsequent discharges. The same problem existed in the double flash equipment; however, it was not serious since only one gap was in the circuit when the second gap fired. In the Type 2307 equipment, a slightly larger capacitor on the second flash circuit equalizes the light from the two flashes.

A mercury-arc control tube (General Electric Connectron No. 1) was tried in the multiflash equipment and served effectively as a switching tube at a 100-kc rate, the energy per flash being about 1.5 wsec. The equipment used to drive the EG&G FX-2 flash tube is shown in Fig. 5. The FX-2 was damaged by overheating when flashed 20 times at a 1-kc rate with 9 wsec of energy; at 1.5-wsec/flash operation it was good up to 100 kc. Other tubes were tested with varying degrees of success. However, in maintaining the light output and duration for successive flashes, the FX-2 was superior to the other tubes. The FT-218, for example, has a much longer flash duration for successive flashes after the first.

As measured with a Type 935 phototube and recorded on a cathode-ray oscillograph, the FX-2 showed 20 distinct flashes, each of 1-μsec duration. The light output per flash was not, however, constant, the second flash being about 25% higher in intensity than the first. Subsequent flashes decreased in intensity, until the output from the last one was only about 50% of that from the second one. It is believed that this variation in light from flash to flash is due to temperature and pressure wave effects in the xenon gas.

On rare occasions a mercury-arc tube failed to deionize and then one or more of the flashes would lose intensity.

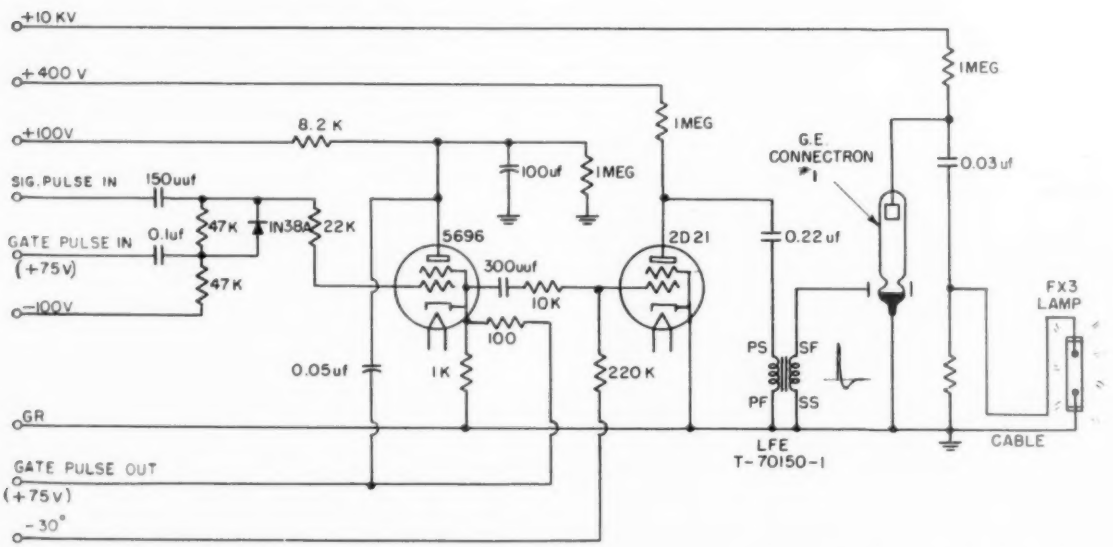

Fig. 6. Gating and triggering circuit as used for each component circuit of the multiflash equipment of Fig. 5. The rate-setting oscillator is connected to the "signal pulse-in" terminal. The trigger signal from the event is connected to the "gate pulse-in" terminal.

Operation of the tube was consistent for 20 flashes with 1.5 wsec/flash at a 100-kc rate. The power input to the tube during this time was 150,000 w and the total energy, 30 wsec.

An oscillator with a peaking circuit was used to trigger a thyratron circuit at equal intervals. Then a gating circuit, when triggered by some event, started a sequence of pictures at a rate set into the oscillator. Details of the gate and sync circuits are shown in Fig. 6.

The multiflash equipment for photographing bullets appears in Fig. 7. Examples of the photography are contained in Fig. 8; here 20 pictures taken at a 30,000 flash/sec rate show a 22-caliber bullet in flight. A 22-caliber bullet is shown in the seven views in Fig. 9; the photo frequency was 50 kc; that is, 20 μsec between flashes.

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Fig. 7. The 20-flash unit. A separate panel is used for each driving circuit. There are ten additional panels on the back of the equipment.

Fig. 8. Twenty exposures of a 22-caliber bullet taken at a 30-kc rate.

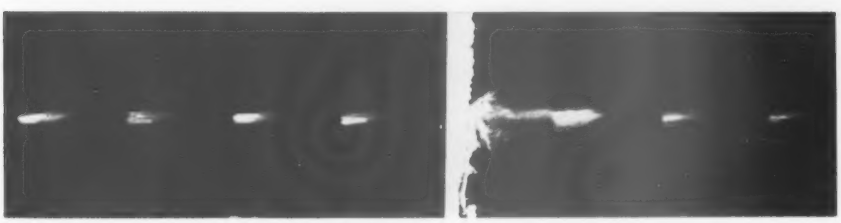

Fig. 9. Seven exposures of a bullet from a 22-caliber Swift made at a 50-kc rate as the bullet strikes a thin paper target. Muzzle velocity of bullet, 4200 fps.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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Automatic Processing of Photographic Code Plates for Electronic Telephone Switching Systems

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Electronic telephone switching systems now being developed require large-scale memories with high-speed random access. This memory is provided by the flying spot store which stores information in binary code in the form of tiny clear and opaque areas on photographic plates. The information on these plates controls the operation of the telephone office and keeps track of the correlation between telephone directory numbers and the location of the line terminals in the telephone office to which these numbers have been assigned.

Periodic changes in the stored information require preparation of new plates. After exposure in the flying spot store, the plates are subjected to a 15-step reversal process in the automatic plate processor. The processor handles one or two plates at a time and is highly reliable, even when used by personnel with little or no photographic training.

Tiny photographic images on glass plates are making possible a new kind of telephone switching system, currently under development at these Laboratories. The new switching system is built around electronic principles, incorporating such devices as transistors, solid-state diodes, and vacuum tubes, as well as such photographic components as lenses, sensitized plates, and automatic processing equipment. In present machine switching systems for dial telephones, the principal building blocks are relays and electromechanical switches, and photography plays a less conspicuous role, chiefly in recording of data.

The System

In the electronic switching system, as in all dial systems, the switching function is performed by a switching network (Fig. 1). This network consists of a complex maze of switching elements, such as step-by-step switches or crossbar switches in some present systems which carry these names, or gas-filled diodes in the new electronic system. All telephones served by the office have connections to the switching network and any two can be interconnected by closing the proper combination of switches or by breaking down the proper combination of gas diodes to form a conducting path. In addition to direct telephone lines, a large variety of "trunks" also have connections to the network. Some of these trunks consist of lines to other communities, lines to operators for those needing assistance in placing their calls, and lines to various tone signals such as the familiar "dial tone," "busy tone," etc. Any telephone line may be connected with any of these trunk lines through the switching network.

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The main function of the rest of the system is to control the switching network so that the proper interconnections will be made at the proper times between different telephone lines and between telephone lines and trunks. This "auxiliary" equipment is in reality a digital computer and comprises more than half the equipment in the electronic office. It has access to each line and trunk, from which it receives electrical signals indicating whether or not current is flowing in each. Current flow takes place at any time the telephone handset is raised except for brief intervals during dialing.

The central control, which receives these signals, is served by two types of memory units: temporary and semipermanent. Information which may change from moment to moment, such as the busy or idle status of each telephone line, is stored in the barrier grid store temporary memory in the form of tiny charged or uncharged areas on the mica target of an electrostatic storage tube of the barrier grid variety.

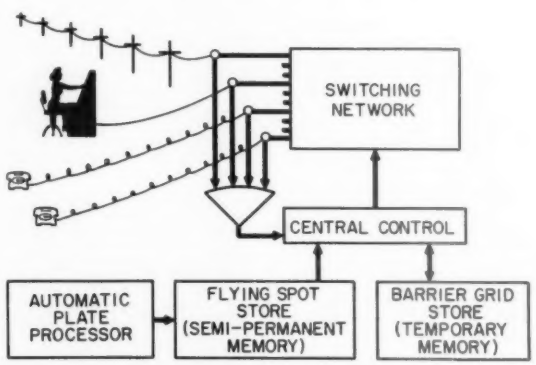

Fig. 1. Electronic switching system.

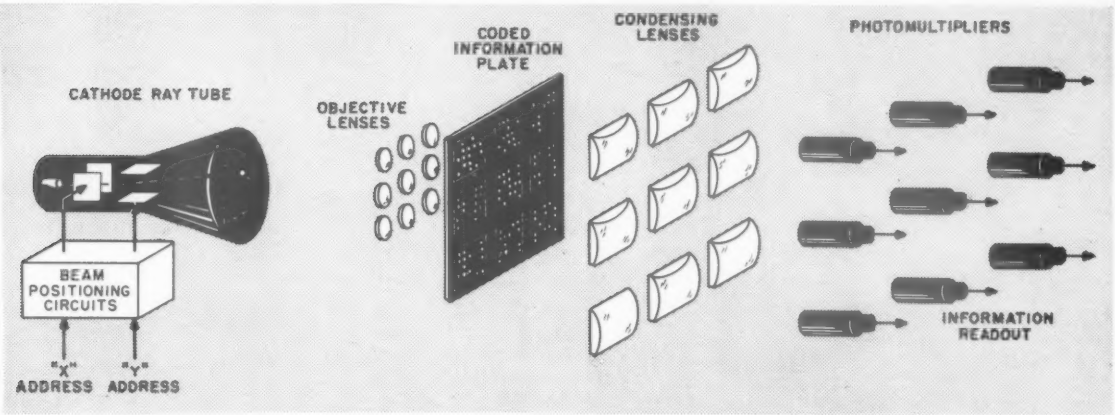

Fig. 2. Flying spot store — simplified diagram.

The central control can send signals to the barrier grid store, instructing it to remember new information as well as to recall the old. For example, the number being dialed by a customer is stored in binary code, digit by digit as the dialing progresses so that when dialing is complete the entire number will be available as needed to set up the proper connections.

Information which is needed for longer periods of time and which does not have to be "written in" or changed at a moment's notice is stored in the flying spot store semipermanent memory. The information is stored in tiny binary coded clear and opaque spots in a number of areas, or channels, on a photographic plate. For simplicity, Fig. 2 shows nine such areas with 25 spot locations in each, although stores have recently been built for experimental use* with 32,768 information spots in each of 68 areas (2.2 million information bits) divided among four different photographic plates. Each area, or channel, has an associated objective lens, condensing lens, and photomultiplier with readout circuits. To read information from the store, the central control sends a particular x, y address to the beam-positioning circuits which deflect the electron beam to this location on the face of the cathode-ray tube. The spot of light is projected by each of the objective lenses to the corresponding address in its associated area on the plate. Light striking each area passes through the plate or is blocked, according to whether the spot previously encoded at that address is clear or opaque. If clear, the light is gathered by the condensing lens and directed to the associated photomultiplier, which gives a positive output signal identified as a binary "1." Lack of output is considered a "0." For example, with the beam directed as shown in the figure (to the position $x = 2$, $y = 2$ in each area), the readout from the photomultipliers would be 10100-1110, reading from left to right and from top row to bottom row. Thus, a large number of binary digits may be read out simultaneously for each address position of the spot on the tube face. With high-speed vacuum tube circuits now being used, a new address can be sent to the store and the new readout information received by the central control in as little as 2.5 μsec. This high speed random access to millions of bits at relatively low cost makes the flying spot store unique among storage systems.

The optical system of an experimental store of the type which will be used in the Morris office is shown in Figs. 3 and 4. A spot of light approximately 0.018 in. diameter on the face of the special experimental cathode-ray tube is positioned to any of 32,000 addresses over an area 5.4 in. square. This spot is projected through 68 objective lenses onto the 17 storage areas on each of four plates. The relative spacing of the tube face, objective lenses, and photographic plates results in a 4:1 reduction in the image size. The storage areas are thus 1.35 in. square and the projected

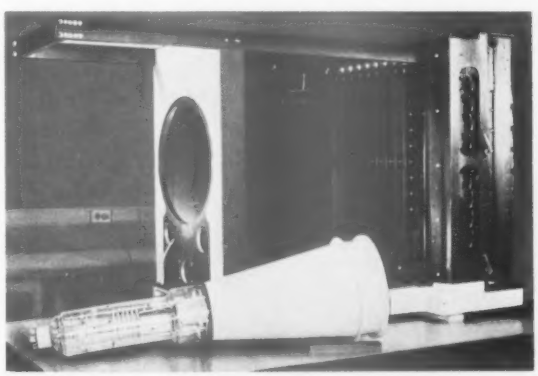

Fig. 3. The flying spot store optical system, containing an experimental cathode-ray tube (shown detached and with shield removed), a field of objective lenses with coordinate shutters for use during plate exposure, a group of four 17-channel information plates, and a field of condensing lenses partially visible at the right end.

*In the Morris, Ill., telephone office.

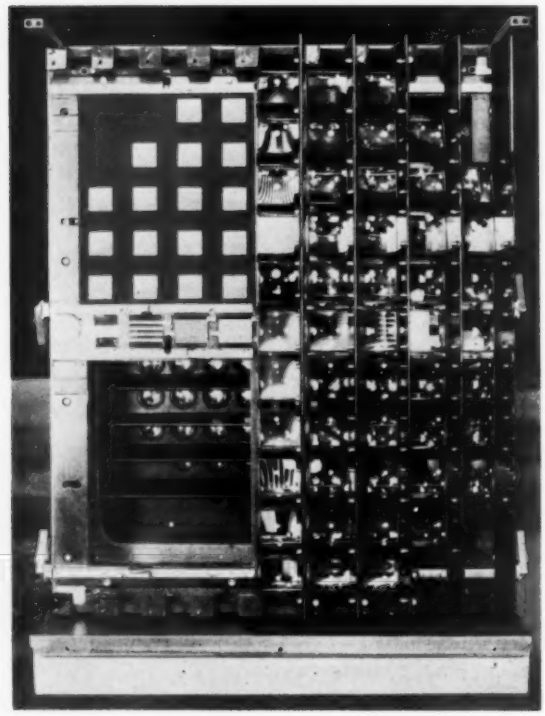

Fig. 4. End view of the optical system with the condensing lenses removed from the left side, showing one of the 17-channel information code plates (above) and some of the objective lenses and coordinate shutters (below).

spot size is approximately 0.005 in. with spot positions on 0.0075 in. centers.

The projected image of the cathode-ray tube (CRT) spot must be accurately positioned in register with the coded pattern on the plates. This is accomplished by an electrooptical servo system which measures the location of the spot image and sends a correction signal to the CRT deflection circuits which drive the spot in the proper direction until the measured and desired positions agree. The method by which this is accomplished is described in another paper to be published in this journal.* The smaller plates with bar patterns just below the 17-channel information plate in Fig. 4 are used, together with others behind the condensing lenses at the right, in measuring the spot position.

In principle, the encoded pattern on the information plates could be obtained by any method which would produce tiny clear areas (binary 1's) in precisely the desired locations on an opaque background. Practicably, the flying spot store itself is ideally suited for this purpose. An unexposed photographic plate is

* M. B. Purvis, and G. V. Deverall, "Photographic Problems Associated with the Construction of a Large Computer Memory," presented at the National Conference, Chicago, 26 October 1959.

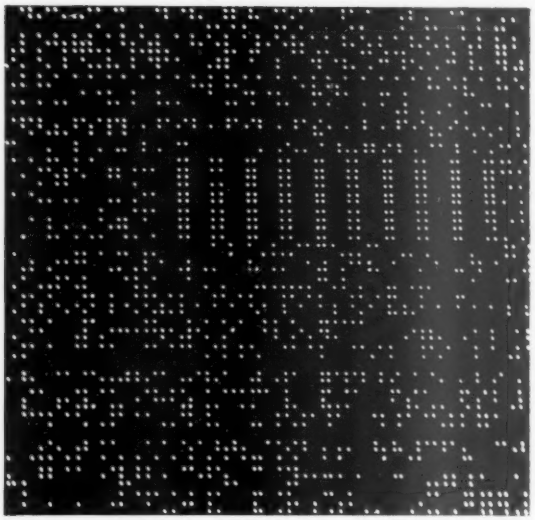

Fig. 5. Enlarged view of a portion of one information area, showing binary encoding.

inserted in one of the quadrants. The vertical and horizontal coordinate shutters on either side of the objective lenses are adjusted to permit light to pass through only one objective lens, and the CRT spot is programmed to move sequentially to each coordinate location, pausing at those locations at which a "1" is to be written and passing rapidly by those positions where no exposure is to be made. This is repeated for each of the remaining 16 channels until all 1's have been exposed. Automatic control of the shutters and CRT spot position permits exposure of an entire plate containing 550,000 spot positions (perhaps half of which require exposure) in less than 3 min. A specimen of a portion of one of these plates is shown in Fig. 5.

After exposure, the plate is removed from the store and given a special reversal process which produces circular, clear areas at each exposed position. For use, the plate is then reinserted in the store to within 0.0002 in. of its initial position during exposure. This is accomplished semiautomatically with the help of precision bearings which engage ground edges of the glass plate.

In the electronic switching system, two kinds of semipermanent information are encoded on the photographic plates. Three of the four plates contain program information which directs the central control (which has limited amounts of expensive logic circuitry and is therefore relatively unintelligent) through its operations. The fourth plate contains translation information with which the desired telephone directory number, recorded in binary code in the barrier grid store, is translated into another binary number which identifies the terminal on the switching network to which the corresponding telephone line is attached, and to which a connection must be made. The program information is changed only when a rare

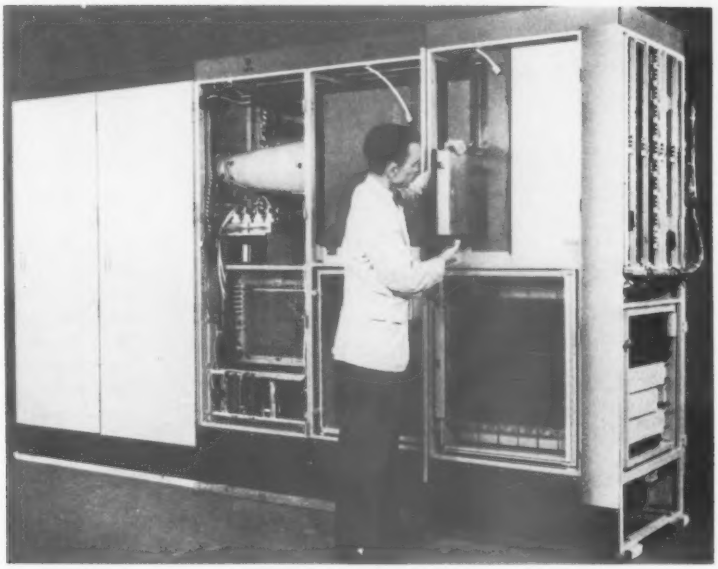

Fig. 6. A plate is inserted into the flying spot store optical system prior to exposure. The two cabinets at the left contain power supplies and part of the cathode-ray tube. Other cabinets contain the store circuitry, as well as the optical system. The photomultiplier tubes and associated circuits are plugged into the end of the right cabinet, in alignment with the condensing lenses of the optical system.

change in mode of office operation is adopted. The translation plate must be changed more frequently, whenever a number of lines are to have a change in associated numbers in the telephone directory. This might be once a month in a small community; more often in a metropolitan area.

The Processor

After exposure in the flying spot store, the plate is withdrawn into a special plate holder, or cassette, which protects it from light and dust (Fig. 6). It must then be processed under conditions of maximum cleanliness and reliability by personnel with little or no training in photographic techniques. For this purpose an experimental automatic plate processor, suitable for use without a darkroom, has been designed and built. The machine (Figs. 7 and 8) handles one or two of the 10 by 12½-in. plates at a time. A carriage receives the plate from the cassette and carries it from one to another of a series of proc-

Fig. 7, *left*. R. F. Glore, one of the designers of the processor, about to attach cassette containing an exposed code plate to one of the two loading stations. After insertion, the plate will be subjected to a special 15-step reversal process to bring out the encoded image.

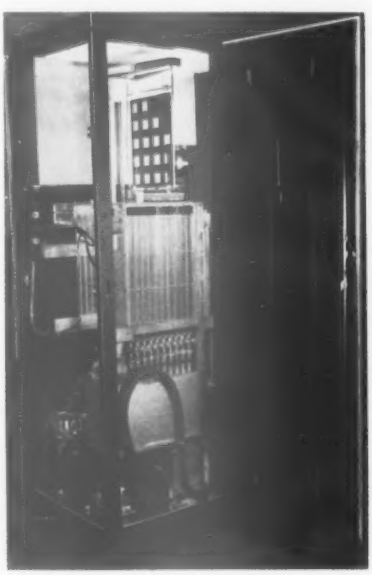

Fig. 8, *right*. Processor, showing plate carriage and processing tanks. There are also lights in the top for re-exposure during processing, a small diaphragm-type air compressor for the gaseous bursts and vertical carriage drive, a sump and pump for disposing of waste chemicals, and a high-efficiency air filter for use with the drying chamber.

TABLE I

Typical Processing Procedure for Plates with Eastman Kodak Co. Experimental Type 55-1 Emulsion

	Step	Tank No.	Time, min
1	Kodak D-19 Developer	3	4
2	Acetic acid stop bath	4	½
3	Etch (equal parts EB2, 3% H_2O_2)	5	3
4	Water wash; expose to light	6	2
5	Redevelop	3	4
6	Stop bath	4	½
7	Kodak Rapid Fixer with Hardener	8	2
8	Water wash	9	½
9	Kodak Farmers Reducer	10	1½
10	Water wash	9	½
11	Fix	8	2
12	Water wash	7	2
13	Fresh water wash	2	1
14	Rinse in detergent	1	½
15	Dry	Dryer	6
	Total Time		30

essing tanks according to a preset program, with individual timing of the dwell period in each.

While there are as many as 15 steps in a typical reversal processing cycle (see Table I) the machine is simple to use and has few external controls. After clamping the cassette with a lighttight seal to one of the loading stations, the machine is prepared to receive the plate by directing the carriage to the appropriate load station with the select knob on the control panel. The white plastic bar on the edge of the cassette is then drawn backward, withdrawing steel tapes which seal the front of the cassette and the entrance slot of the processor, permitting injection of the plate into the processor by means of the handle on the side of the cassette. Processing is then started and continues automatically until completion, which is signaled by the lighting of a lamp.

The plate carriage is actuated vertically by compressed air in an air cylinder and horizontally by a motor-driven screw. Precise horizontal positioning over each tank is obtained by disengaging a half-nut

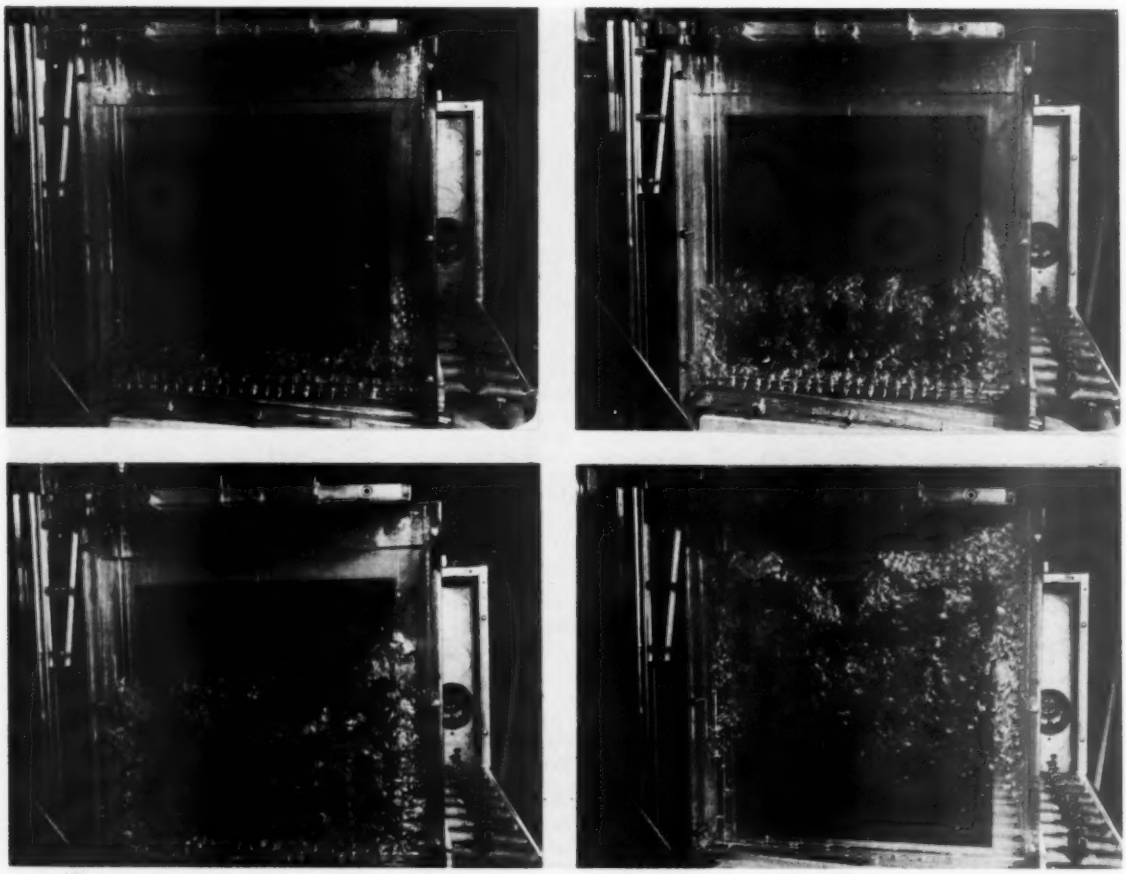

Fig. 9. View of an early model of the processor, showing the progress of a burst of bubbles from the plenum at the bottom to the surface of the chemical solution.

from the lead screw and sliding a nylon fork into engagement with an accurately located pin. This avoids the need for stopping the motor and drive screw at any precise position, which would be difficult because of inertial effects.

The processing tanks are made of methyl-methacrylate for corrosion resistance and hold ½ gal of chemical solution each. The machine contains 11 tanks for chemicals. The plates can be inserted into ten of these but the eleventh is short and is used to hold the "B" solution of the Farmers Reducer needed for Step 9. This must be mixed with the "A" solution in Tank No. 10 just before use because of the short life of the mixture. The mixing is accomplished by means of an automatically actuated solenoid valve which allows the "B" solution to flow into Tank No. 10 at the appropriate time in the process. The conveyor supports the plates 0.4 in. apart, with emulsion sides facing each other. The tanks are just wide enough to receive this assembly with minimum clearances between the sides of the tanks and the uncoated glass surfaces.

During processing, the solutions are agitated by the "gaseous burst" method, in which bursts of air bubbles are allowed to stream upward between the plates. The burst duration and the interval between bursts are adjustable and controlled by an electric timer. Typical values of 1.2-sec burst and 12-sec interval have been found to give effective agitation with sufficient time to allow the bubbles from one burst to rise to the surface and associated currents to become quiescent before the succeeding burst arrives (Fig. 9). This is necessary to achieve randomness of agitation, since otherwise circulating current patterns may be established in the solutions with resultant nonuniform processing. In the automatic processor, the bursts for all tanks are supplied from a single stainless steel tube which forms part of the plate carriage and is transported from tank to tank with the plates being processed. An almost uniform burst pattern is obtained by feeding compressed air into both ends of the tube. It is not necessary to use nitrogen or other nonoxidizing gas for the bursts because of the limited number of plates, seldom more than four, processed in a given period. For reliability, fresh chemicals are used for each occasion on which new plates are to be made.

The compressed air for the bursts is supplied by a small diaphragm-type air compressor (Fig. 8, lower left). This type was chosen to eliminate the possibility of injecting oil and other impurities into the filtered air. The air flow for the bursts is controlled by an intermittently operated solenoid valve in series with a small pressure-reducing valve. When in the down position, the carriage is linked to the air supply by means of a stainless steel tube which engages a nylon cylinder with an O-ring seal. A small check valve rides with the carriage to prevent reversal of air flow and consequent chemical contamination of the tube from which the bursts are emitted. The compressor also supplies air for the main cylinder which raises and lowers the plates, and for a second cylinder which removes the half-nut and drives the tapered fork into engagement with the horizontal positioning pins. The compressor noise is reduced to a low value by vibration mounting and by use of a muffler in series with the intake.

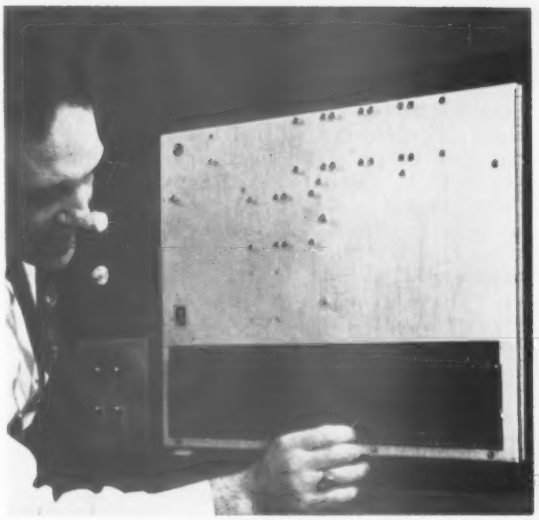

Fig. 10. A pin is inserted in the timing section of the program panel to select the dwell time for one step in the cycle. Other pins determine other variables, such as the particular tank to which the carriage is directed for each step.

The plates are dried by rinsing in a mild detergent which minimizes formation of droplets and by circulating filtered, warm air past the plates in a drying chamber adjacent to Tank 1. The air is blown downward past the plates to help carry away droplets which naturally run downward by gravity. This minimizes spotting due to drying of droplets within the image areas.

The processor contains a very versatile program panel from which the steps and timing of almost any desired process may be easily set up or changed (Fig. 10). The tank or position to which the machine is directed and the precise time it will remain there are determined by merely inserting gold-plated pins in the appropriate holes. Similarly, other pins may be inserted to establish the time at which solutions are mixed (Tanks 10 and 11), when lights are turned on in the processor for exposure during processing, and when the blower and heater are turned on for drying. To simplify the circuitry, pins must also be inserted to indicate whether the desired tank location is to the left or right of the present location. The timing circuit uses relays and selector switches to count revolutions of a shaft which is rotated at the rate of once every six seconds by a synchronous motor. The counter and shaft start over from a zero position when the carriage is lowered, so that the carriage transit time does not affect the dwell time, and adjustment of the time interval for one step of the process does not change the timing for any other step.

The smallness of the clear areas on the processed plate requires that the plates be essentially free from dust or other particles before exposure and that this cleanliness be maintained through all subsequent handling and processing. After initial cleaning, the plates are never exposed to room air but are continuously enclosed in the dusttight cassette, the flying spot store, or the processor. The processor is maintained essentially dust free by means of special air filters in the bottom. As long as the door is closed, virtually all air entering the machine passes through these filters, including air used for the gaseous bursts, air cylinder operation, and drying. The filters used are of a pleated glass-asbestos type which are more than 99% efficient in removing dust particles larger than 0.3 μ. While occasional particles a hundred times this size would probably not be objectionable on the code plates, the finer filtration provides margins against flocculation (the formation of large particles from aggregates of smaller ones) within the processor.

The processor contains a number of interlocks and other safety features to protect the mechanism in the event of malfunction or improper handling. Mechanical interlocks prevent closing the lighttight steel tapes preparatory to starting the cycle unless the plate is fully inserted into the machine. Limit switches at the ends of the normal travel for the plate carriage disable the screw drive, in the event that this normal range of motion should be exceeded for any reason. The vertical carriage drive is not permitted to lower the carriage at any station until closing of a switch signals that the pin for precise horizontal positioning has been fully engaged. Once the process cycle is started, all external controls are disabled until the cycle is completed, with the exception that depressing an emergency "home" button will return the carriage at once to one of the loading stations. The design of the processing tanks with sump and drain pump make cleaning easy, thereby minimizing opportunities for contamination due to accumulated chemical deposits.

The experimental model of the processor described here has been used on many occasions for processing plates for the flying spot stores. It appears to meet the objectives of more uniform, more reliable processing than can be achieved readily by hand methods, and to do this easily, without a darkroom, under control of personnel with little or no background in photographic techniques.

Acknowledgments

The electronic switching system has been developed by a large number of people under the direction of C. A. Lovell and R. W. Ketchledge. The automatic processor was developed by R. K. Eisenhart and R. F. Glore. The author also wishes to acknowledge valuable assistance from consultants at Eastman Kodak Company, who have helped with nearly every aspect of the photographic problem.

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Photosensitive Materials for the Preparation of Molded Photosurface Terrain Models

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Described are photosensitive materials that retain sensitivity during a heat molding cycle and subsequently can be given photographic exposure by orthogonal projection to produce a master negative which can then be used for contact printing on a similarly molded photosensitive material. The master negative stock is silver-halide sensitized, and the print material is iron-salt sensitized. Each type of emulsion is prepared with polyvinyl alcohol and is coated on a film base having the required heat-molding capability.

A "photosurface terrain model" is a detailed photographic facsimile of the earth's surface in the form of a three-dimensional scale model. Such models are prepared by means of a long sequence of techniques, beginning and ending with the photographic process. The original terrain is surveyed by photogrammetric engineers whose dual flight patterns supply the original data. Computations are then made, leading to the construction of the scale-model equivalent of a topographic map, except that the "map" is not drawn as a two-dimensional representation of the original three-dimensional terrain. Instead, the data are set up in a computer and fed to a router which cuts out the contours of the original terrain in a block of plaster. This is the original "terrain model," and it must be reproduced in contour facsimile by a photosensitive film upon which can be printed the photographic detail of the original photogrammetric negatives. This means, in effect, that by aerial photography one can reconstruct the hills to scale and then, by further use of the photographic technique, return the trees to the hills! The U.S. Naval Training Device Center has pioneered in the development of this technique.

This paper discusses only the experimental preparation of photosensitive materials for the molded master negative and a print film. The speed of the molded master negative film must be sufficient for projection printing; that of the final print stock may be of contact-printing speed after heat molding.

The film base must be selected for its heat-molding capabilities within the temperature range 100°–140°C; the emulsion coating must retain good adhesion during the heat-molding cycle, and thereafter through photographic processing and drying.

Printing of the master negative is by orthogonal projection. This means that the image is received on the three-dimensional film area from a collimator beam without distortion. Final printing is by contact of the molded master negative with a similarly molded photosensitive material.

The early portion of this study was directed toward the photosensitization of a polymeric coating for preparation of the final print film. To this end, a number of light-sensitive systems were investigated, including diazo, metal diazonium salts, zinc oxide-silver nitrate, and iron salts. The polymeric binders studied included polystyrene, polyvinyl acetate, and polyvinyl alcohols.

The diazo and metal diazonium systems were discarded, as was the zinc oxide-silver nitrate, because of unfavorable stability during the heat-molding cycle, with consequent loss of photosensitivity.

Three iron-salt sensitizing systems were investigated. All of these depend primarily on the photolytic reduction of ferric to ferrous ions by ultraviolet and blue-violet exposure. Thereafter the application varies. In the first variation the photolytically reduced iron salt can be made to react with polyvinyl acetate when heated. This alters the hydrophilic-hydrophobic properties of the polyvinyl acetate surface. Thus the developed image area rejects aqueous inks and dyes and gives rise to a direct positive system. The difficulty in use of this process for the present application stems from the fact that the material must be amenable to heat molding, *followed* by photographic exposure and development. Exposure of this material to heat during the preliminary molding operation caused almost complete loss of sensitivity to light.

Presented at the National Conference, Chicago, 26 October 1959. Received 1 July 1959. The work reported here was performed under Contract N 61339-57 for the U.S. Naval Training Device Center, Port Washington, N.Y.

The second variation utilizes the photolytically reduced ferrous ion to harden polyvinyl alcohol in the presence of hydrogen peroxide. The image area remains as a wash-off relief, but the differential hardening is not great, and the system is not easy to use on this account.

The third iron-salt sensitized system is a modification of the old Kallitype process. In our adaptation, ferric ammonium citrate or oxalate is combined with polyvinyl alcohol in aqueous solution for coating on the heat-moldable base. Contact exposure through a molded master negative, using a light source high in ultraviolet, is followed by physical development with silver nitrate.

The unexposed films show good stability to the heat-molding cycle, offer excellent molding capability, and are developed easily — and almost instantaneously — after the photographic exposure, to give a very stable final image of silver. The material may be conveniently handled in low-level tungsten illumination without fear of fogging, although fluorescent lighting in the work area may give trouble.

A formula for the preparation of an iron-salt sensitized polyvinyl alcohol coating material is as follows:

10% aqueous "Elvanol" 52-22	100	grams
15% aqueous Ferric ammonium oxalate	50	grams
Parez Resin-613 (melamine-HCHO hardener) (American Cyanamid Co.)	1.0	gram

This composition may be coated on polyvinyl chloride or other heat-moldable base at 0.0015- or 0.003-in. wet-thickness. The addition of the melamine-formaldehyde resin effects hardening of the coating during the molding heat treatment.

After photographic exposure, such coatings can be processed in the following physical developer composition:

Distilled water	200 ml
Silver nitrate	4.0 grams
Ammonium hydroxide sufficient to redissolve the precipitate first formed	
Sodium sulfite	0.4 grams
Boric acid	0.3 grams

Develop for 30 sec, rinse, fix briefly, wash, and dry.

The Molded Master Negative

In the preparation of a photosensitive heat-moldable master negative, the requirement of sufficient speed for projection printing necessitates the use of a silver halide emulsion. This poses a problem of an entirely different order from that of preparing the print material, although the problem still retains some of the same parameters, such as retention of photosensitivity after undergoing the heat-molding cycle. This requirement rules out the use of gelatin emulsions, since gelatin does not respond favorably to elevated temperatures.

For our present purpose, a rather simple silver halide emulsion may be prepared by precipitating the silver halide in a 1.5–3% aqueous solution of polyacrylamide at 50°C, then adding polyvinyl alcohol which contains 1% or less of polyvinyl ester. The polyacrylamide dispersing agents used were obtained by courtesy of the American Cyanamid Company, and the polyvinyl alcohol was "Elvanol"-72-60, supplied by E.I. du Pont de Nemours & Co.

The selection of "Elvanol"-72-60 was made in the belief that this product, which is essentially cold-water insoluble, would be cold-water resistant enough to withstand processing, as in ordinary photographic procedures. Other "Elvanols" such as 52–22, having a higher polyvinyl acetate content and lower viscosity, work equally well in the preparation of the emulsion but tend to wash off the base during processing because of their cold-water solubility.

A typical emulsion is prepared as follows:

Five grams of polyacrylamide PAM-50 are dissolved in 200 ml distilled water at 50°C. To this aqueous solution, Solutions A and B are added simultaneously through twin jets while the mixture is being stirred in a constant temperature bath at 50°C.

A.	Silver nitrate	10	grams
	Distilled water	40	cc
B.	Potassium bromide	7.5	grams
	Potassium iodide	0.25	grams
	Distilled water	40	cc

The precipitation time is accurately controlled by pouring Solutions A and B into separate jet tubes, formed by sealing short lengths of capillary tubing on 4-to-5-in. lengths of 20-25 mm ID glass tubing.

Before the actual precipitation, 150 grams of a 7% aqueous solution of "Elvanol"-72-60 containing 5 cc of concentrated ammonium hydroxide is heated to 50°C.

Following the precipitation — which requires about 1 min 20 sec — the suspension is stirred for 5 min in the constant-temperature bath. Then the ammonia-polyvinyl alcohol solution is added slowly over a period of 1 min and the emulsion stirred for 20 min at 50°C.

The emulsion, for non-washed application, may now be removed from the constant-temperature bath, filtered through 100-mesh nylon bolting cloth and coated immediately at 40°C.

For small sample experimental coatings it was found expedient to use the Bird Film Applicator. This is comprised of a vacuum hold-down plate and a doctor-knife emulsion spreader set at 0.003 in. The coated sheets are placed in dry boxes for room-temperature drying.

This emulsion, when coated out at 0.003-in. wet-thickness and dried, was given a standard exposure and development. Samples were subjected to humidity test for accelerated aging for 100 hours at 130°–134°F and 100% RH. The material, retested at the standard conditions, showed a slight gain in fog density with negligible loss in speed.

A sample of the emulsion was allowed to stand at room temperature for 10 days. A large proportion of

the suspended halides had settled out, but the silver salts were easily redispersed by agitation. Coatings from the redispersed emulsion at the 0.003-in. thickness were exposed and processed under standard conditions. A gain in speed of about one stop had occurred without measurable gain in fog density. The material molds well and after the heat-molding cycle is clean working.

If the emulsion is coated on 10 mil polyvinyl chloride film base, the resulting photosensitive element may be molded under an infrared lamp at 110°–120°C, using a 5-min heating period.

For coating on polyvinyl chloride sheeting, a substratum layer was found necessary to provide suitable anchorage of emulsion to base. Polyvinyl butyral resins, coated from an alcohol-ketone solvent system, were found to give good results, with excellent adhesion. The degree of bite of the substratum can be controlled by raising and lowering the ketone content.

When coated on polyvinyl chloride base, either subbed or unsubbed, these polyvinyl alcohol-silver halide emulsions have very poor wettability and tend to repel, leaving spotty coatings with irregular thicknesses. Addition of saponin to the coating mix eliminates the repellency, and smooth, even coatings result.

To protect the surface from scratching during the heat-molding operation, an anti-abrasion coating can be used on top of the silver halide-polyvinyl alcohol emulsion. This consists of a 0.5 to 1.0% solution of the same polyvinyl alcohol used in the silver halide mix. A melamine-formaldehyde resin, such as Parez-613 from American Cyanamid, is added to the anti-abrasion layer to the extent of 50% of the dry weight of the polyvinyl alcohol. The excess melamine formaldehyde diffuses into the emulsion and provides some insolubilization of the emulsion layer.

Test Negative Mold

For test purposes, a small plaster-of-Paris negative mold of the terrain model was prepared. This has perforations at the deepest points of each contour. All of the perforations are connected to a vacuum chest which is, in turn, connected to a source of vacuum. When a test film is taped to the mold and heated by infrared, with the vacuum turned on, the film assumes the contours of the mold. Then the heat is removed while the vacuum is sustained until the film and mold cool. Thereafter the photosensitive molded film may be photographically exposed, processed, and dried by the usual procedure.

Since it may be desirable to increase the initial speed of the basic emulsion, a gelling agent may be added and the emulsion chilled and set for noodling and washing. The washed noodles may then be remelted, the appropriate sensitizers added, and the emulsion digested. The stabilizers and coating aids are then added, and the emulsion coated and dried. The extent to which the photographic characteristics of the finished emulsion must be modified will dictate the treatment required for sensitization.

Acknowledgment

We wish to thank the Naval Training Device Center at Port Washington, N.Y., for the contract support which has made our investigation possible, and also Robert Entwistle of NTDC for permission to publish this report.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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A Nomograph for Selecting Light Balancing Filters for Camera Exposure of Color Films

C. S. McCamy, *National Bureau of Standards, Washington, D.C.*

A nomograph has been designed for rapid selection of filters to adjust the spectral quality of the illumination to the spectral sensitivity of the film for color photography. The nomograph provides for a very large number of combinations of films and light sources in a simple form, permits the easy interpolation of new films, light sources, or filters, indicates which filters would nearly satisfy when an ideal filter is not available, indicates the general nature of abnormal combinations for special effects, and provides a convenient conversion from color temperature to reciprocal color temperature. The nomograph is based on the assumption that the color balance of color films, the chromaticity of the illumination, and the effect of filters can be characterized adequately on a scale of reciprocal color temperature and that the change of reciprocal color temperature by a given filter is a constant.

Generally, the most satisfactory color photographs are obtained if the spectral sensitivity of the film is balanced for the spectral quality of the illumination. However, it frequently becomes necessary to use film which is not properly balanced, either because there is no available film balanced for the light to be used or because it is not practical to change films once the camera is loaded. It is common practice in such cases to place a colored filter over the camera lens to adjust the spectral quality of the light to the spectral sensitivity of the film. There are many such filters commercially available to adjust a variety of light sources to the various color films. Manufacturers of films and filters publish tables indicating which filter to use with a given combination of film and light source. The nomograph described herein serves the same purpose as such tables but is more useful in that it provides for a very large number of combinations in a simple form; permits the easy interpolation of new films, sources, or filters without altering the rest of the chart; gives an approximate solution to the problem when there is no exact solution; and indicates the nature of abnormal combinations which might be employed for special effects.

The Nomograph and Its Use

The nomograph is shown in Fig. 1. Various light sources and their correlated color temperatures in degrees K are listed on the left, various filters and their correction effects in micro-reciprocal-degrees (mireds) are listed in the center, and various films are listed on the right, with the type of source for which they are balanced given in mireds. If a straight edge is placed on the points corresponding to a film and a light source, the edge crosses the center line at the point corresponding to the appropriate filter. The point on the filter scale corresponding to zero-correction indicates that no filter is needed since it lies between the points representing any film and the light source for which it is balanced.

Filters above the zero-correction point (+) are yellowish or orange in color; those lying below (−) are bluish. If the point corresponding to the filter actually used lies above the indicated ideal point, the resulting photograph will be generally yellower than normal. If the filter actually used falls below that indicated, the photograph will be bluer than normal. The extent of these effects can be visualized approximately before the picture is taken by viewing the scene momentarily through a filter having the same correction effect in mireds as the difference between the indicated ideal correction and that of the filter to be used on the camera. The correct algebraic sign for the viewing filter is obtained by subtracting the value for the ideal filter from that for the filter to be used on the camera.

The nomograph may be used to convert color temperature to mireds and vice versa. The sources are listed on a graduated scale of color temperature, the films are listed on a scale of mireds, and any line through the zero-correction point connects corresponding points on these scales.

Sources having spectral radiation characteristics markedly different from those of ideal radiators are indicated with a superscript "b." In such cases, correlated color temperature is not an adequate specification of color for use in color photography but gives an approximation which may be useful.

The data on which Fig. 1 is based were taken from numerous sources, mostly the published recommenda-

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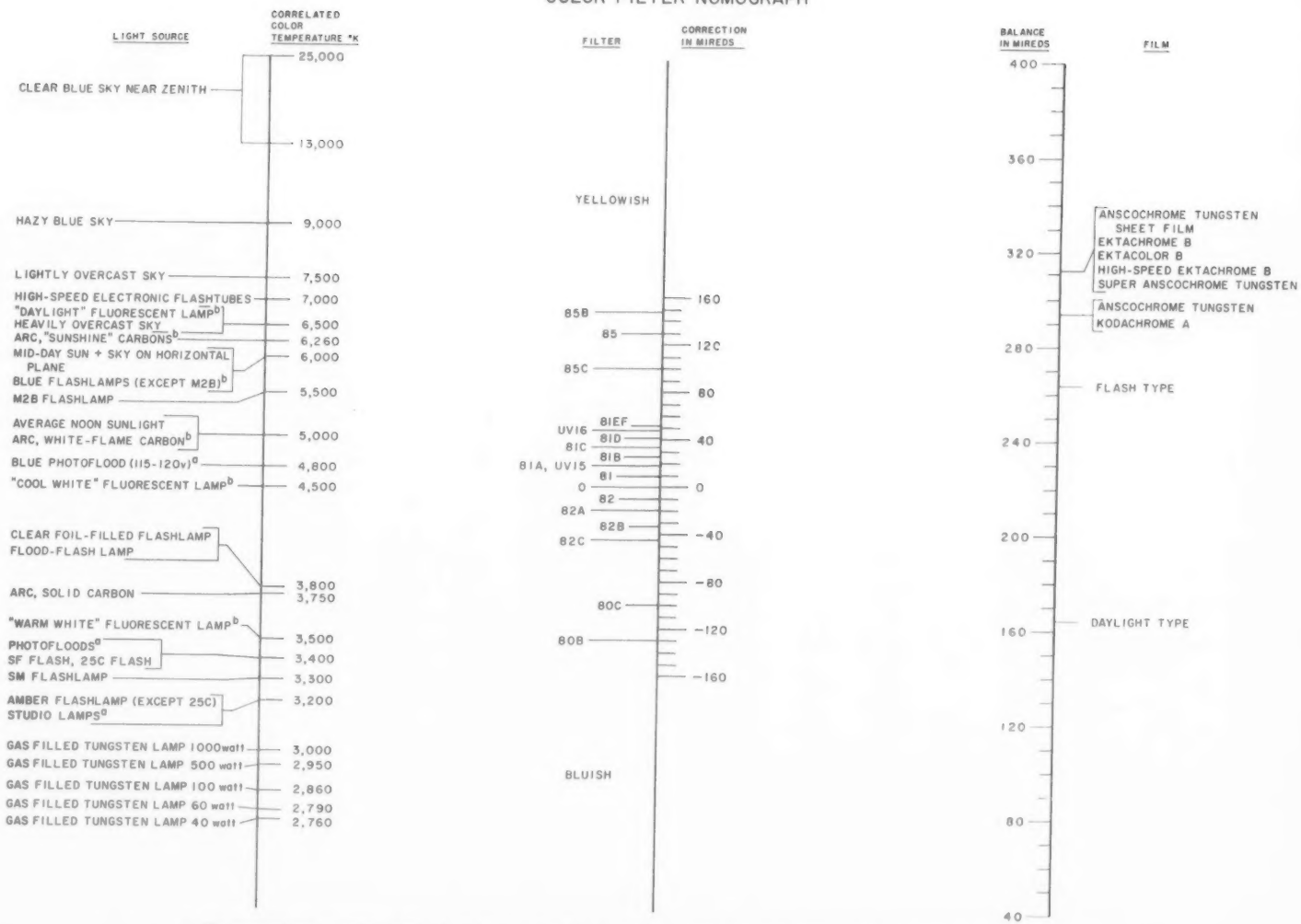
COLOR FILTER NOMOGRAPH



a- The correlated color temperature of these lamps increases about 11°K for each volt increase in applied potential, in the neighborhood of 115v. As lamps are used, the correlated color temperature (at a given voltage) decreases, often from 50°K above to 50°K below the rated value during the life of the lamp.

b- Color temperature is only an approximate specification of these sources.

Figure 1

tions of manufacturers of films, lamps, and filters. The Wratten filter designations were used, for the most part, because of their general usage in photographic technology. Filters designated according to reciprocal color temperature may be selected by use of the filter correction scale graduated in mireds. Although the effects of the various filters could be computed from the known spectral transmittances, the values assigned in Fig. 1 were not obtained in this way. Rather, values were computed from the light source and film combinations for which the filters are recommended. For this purpose, daylight was assumed to have a correlated color temperature of 6100°K. No effort was made to achieve completeness in the nomograph shown, as it was intended merely to illustrate the method.

Theory

Although the colors of bodies are generally described and specified by multidimensional systems, it is sometimes practical to use a one-dimensional scale. One such is the scale of color temperature on which the color of a body is specified by the temperature of an ideal radiator which is of the same color. Since an ideal radiator does not assume all possible colors as the temperature is varied, it follows that not all colors can be described adequately in terms of color temperature. However, the colors of the illuminants generally used in color photography happen to match the colors of ideal radiators sufficiently well that color temperature is an adequate specification for the purpose. (There are a few exceptions to this rule, as noted earlier.) Priest[1] proposed the use of reciprocal temperature, instead of temperature itself, for specifying the chromaticity of incandescent illuminants and various phases of daylight and recommended the micro-reciprocal-degree Kelvin as the most convenient unit. He pointed out that a given small interval on this scale represents an equally perceptible difference in chromaticity regardless of the color temperature.

Gage[2] showed that if the logarithm of the transmittance of a filter is a linear function of wave number, the filter will alter the radiant energy distribution from that corresponding to Wien's equation for one temperature to that for another temperature. Fabry[3] and Langmuir and Orange[4] had suggested earlier that with a given filter designed to alter color temperature, the reciprocal color temperature is changed by the same amount regardless of the color temperature of the source. The present nomograph is based on this fact. It is assumed that the color balance of color films, the color of light sources, and the effect of real filters can be characterized adequately on a scale of reciprocal color temperature.

The accuracy of the method depends, in general, on the degree to which the assumed conditions are met. However, because filter correction values were assigned on the basis of recommended usage rather than on a theoretical basis, the answers obtained necessarily correspond with manufacturers' recommendations in the most-often encountered cases, those cases for which the filters were designed.

The mathematical validity of the nomograph can be shown by the following geometrical considerations. The three scales on the nomograph are parallel and are linear with respect to reciprocal color temperature. The scale for light sources, if given in micro-reciprocal-degrees, would increase downward, that for films increases upward, and that for filters has graduations half the size of the other two scales and passes through zero at the center. The filter scale lies equidistant from the other scales. Given a point A corresponding to some film, a line may be drawn through the "no filter" point D to a point B corresponding to the source for which the film is balanced. Another line may be drawn from A to some other source C, passing through point E on the filter scale. Since the scales are parallel and equidistant, DE is one half BC, but since the filter scale has graduations half as large as those on the light source scale, the number of mireds difference between the light sources is equal to the number of mireds change shown on the filter scale. The same kind of geometrical construction holds for all combinations of films and sources.

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• Book and Journal Reviews

Commercial and Industrial Photography

DAVID CHARLES, The Macmillan Company, New York, 1959. 402 pp. + xi pp., 136 illus., 6 by 9 in., $10.50.

The reader develops a warm regard for the author of this book as he realizes that here speaks a man with more than a generation of experience as a successful commercial photographer. Throughout the book there are described many ingenious devices which David Charles designed as picture-taking aids. Some of them are worthy of note. Except for them, however, the book will not serve as a text for the student or as a manual for the photographer because it is not comprehensive enough in its treatment of each topic. There is much referring to later chapters which do not, when they are reached, add much more specific information. The book lacks illustrations showing how the author's techniques affect his photographs. In places the book is hard to read, too much is said, the point is obscure. There is one important improvement in processing techniques made since the author started his career which he seems to have failed to learn. That is the use of an acid stop bath. He implies that it was only devised so the processor could "jerk" an overexposed negative or print.

Most readers—even his countrymen—will call Charles old-fashioned. Nevertheless the book is well worth reading. The student should read it, not for technical information but for its practical advice. There are numerous suggestions which, if followed, could make one's road to successful photography much shorter and easier. Three of the most interesting Charles calls "Bang the Box," "system in the 'Kit,'" and the "system of 'Silent Signals.'" —*Donald L. Smith, Rochester Institute of Technology*

Image Dissection in High Speed Photography

J. S. COURTNEY-PRATT. Special Issue No. 2, 1958 (in English) of *Photo. Korr.*, Verlag Dr. Othmar Helwich, Darmstadt and Vienna, 38 pp., 29 illus.

There has been a need in the field of photographic literature for a medium whereby extensive authoritative reviews of important subjects could be given prompt publication. The special numbers (Sonderhefte) of *Photographische Korrespondenz* represent just such an outlet. These issues are printed on the same high-quality paper and with the same care that marks the production of the regular issues of *Photographische Korrespondenz*.

The first of the special numbers was a 36-page article by J. W. Mitchell, "Die Photographische Empfindlichkeit (The Nature of Photographic Sensitivity)," published in 1957. In this work, Dr. Mitchell reviewed (in German) his current theories of sensitivity, latent-image formation, and development, with extensive references to the theoretical and experimental results of many workers in the field. A review of this article was published in the August 1958 issue of the *Journal of the Optical Society of America*.

Sonderheft 2, published in English in November 1958, is a well-documented review by J. S. Courtney-Pratt of systems of high-speed photography and cinemicrography based on the principle of image dissection. The author has himself made major contributions to this field, which he entered because a method of ultrahigh-speed photography was needed in studies on explosion and kindred phenonema being carried out at Cambridge University. He writes with the authority of considerable personal experience in the application of the image-dissection method. In this survey, he discusses the general principle of image dissection with its advantages and disadvantages, and describes and evaluates different image-dissection systems, including those of Tuttle, Brookes, Sultanoff, O'Brien and Milne, Young and associates, Courtney-Pratt, Courtney-Pratt and Huggins, Eisner, Langham Thompson, Bray, Viard, and Kühne, as well as that of Lunn and Chippendale, in which the image-converter tube is used. He concludes: "It is because one can see the extent to which one can develop dissection methods in general and the combined image-converter image-dissection methods most particularly, that it is urgent and important to apply intensive development effort to these methods. We are nowhere near their fundamental limits, whereas we are approaching a real and definite limit, the Schardin limit, for the more conventional equipment." — *T. H. James*

The Optical Industry Directory

The Optical Publishing Co., Lenox, Mass., 1959, paper covers, 254 pp., $5.00

Despite the glamour of the new developments in apparatus that extend man's senses into the regions of invisibly short and invisibly long radiations, the continuing importance of optics in its pristine meaning is strikingly shown by this list of some 1200 American suppliers of some 400 types of optical apparatus and parts. These suppliers, including importers, designers, manufacturers, and distributors, are listed alphabetically with their addresses, chief officers, and products. There follows an alphabetic list of types of apparatus, with the suppliers listed by states, and finally comes a list of corrected lenses (especially photographic) that are commercially available in this country. This fifth and completely revised edition of what apparently is intended to be an annual publication is indispensable to anyone who needs anything optical, from abrasive materials to zone plates, that is in the least out of the ordinary. — *F. H. Perrin, Eastman Kodak Co.*

Journal of the Society of Scientific Photography of Japan

Vol. 21, No. 4, December 1958 (in Japanese)

Résumés by T. H. J.

Electron Microscopical Observation of the Effect of Gelatin Envelops on Print-out Process

YASUO SHIMIZU, EIICHI MIZUKI, AND SHIN FUJISAWA, pp. 160–162

Hamm and Comer (*J. Appl. Phys.*, *24:*1495 (1953)) have shown that the silver halide grains of an ordinary photographic emulsion are surrounded by a "silver gelatinate" envelop which survives solution of the silver halide and matrix gelatin and is visible under the electron microscope. The present authors investigated the effect on these envelops of printing out the silver halide grains by exposure to sunlight. Silver bromide emulsions prepared by the neutral process with and without chemical sensitizing were used. Electron micrographs are reproduced showing, for the sensitized and unsensitized emulsions, (A) the envelops of unexposed grains, after the matrix gelatin had been removed with water at 60°C, (B) the same after the gelatin had been removed by enzyme treatment, (C) the envelops of grains which had been partially printed out by exposure to sunlight for 1 hour before removal of the matrix gelatin, and (D) the envelops of grains which had received the same exposure after the matrix gelatin had been removed by the 60°C water. The envelops of the grains which were printed out in the presence of matrix gelatin show areas which are more opaque to the electron beam than the envelops of unexposed grains, and this is attributed to a product formed by action of the photolytic bromine on gelatin. The envelops of the grains exposed in the absence of matrix gelatin are more transparent than those of the unexposed grains, indicating that the envelops are partially destroyed during exposure. The authors conclude that most of the photolytic bromine is accepted in the matrix gelatin surrounding the silver gelatinate envelop when the grains are embedded in a gelatin layer. No difference was noted between chemically sensitized and unsensitized emulsions.

Some Experimental Studies on Photographic Sensitivity

YASUSHI OKAMOTO, pp. 163–170

The first part of this paper deals with measurements of optical absorption by silver chloride and silver bromide, previously reported in *Nachrichten der Akademie der Wissenschaften zu Göttingen, IIa* (No. 14), 275–83 (1956). Absorption spectra of silver chloride and silver bromide in the visible and ultraviolet regions are reproduced for several temperatures ranging from 20°K to 700°K. The second part of the paper summarizes results of reciprocity-failure studies carried out in Eggert's laboratory on experimental emulsions subjected to various forms of chemical ripening and developed in various ways (normal, surface, internal, physical). The experimental results have been reported, for the most part, in more detail in two papers published in the *Zeitschrift für Elektrochemie, 60:* 71–85, 500–507 (1956). Dr. Okamoto discusses the results on the basis of Mitchell's views on sensitivity.

Methods for Reducing Optical Noise in Photographs

MINORU TAMURA AND KUNIO ANDO, pp. 171–175

Several reports have been published on the reduction of optical "noise." They all adopt the method of cutting off the spatial high-frequency component of noise. The method is effective for periodic optical noise, such as halftone dots. However, it does not work well in the case of photographic-grain noise, since the low-frequency components of grain patterns, if emphasized in the formation of the image, give rise to a pronounced graininess effect in enlargements. We have therefore concluded that in order to reduce graininess, the high-frequency components should not be filtered out but should be strengthened, in order to provide as good imagery of the primary grain pattern as possible. A special enlarger utilizing point sources to reinforce the high-frequency components has been constructed, and has been found to give prints of reduced graininess. (*Modified version of authors' abstract.*)

Photographic Pressure Effect (II). On the Hardness of Photographic Materials

YOSHICHIKA KOBAYASHI, pp. 176–180 (Part I published in the *J. Soc. Scientific Phot., Japan, 18:* 104 (1956))

In Part I, it was shown that pressure preceding exposure caused a decrease in surface latent-image formation and an increase in internal image — an effect related to the deformation of the emulsion grains caused by the pressure. In the present paper, the possible relation between the degree of pressure desensitization and the hardness of the gelatin and of the silver halide crystals is investigated. Young's modulus, determined for gelatin film at pH 5.75 and 6.98, decreases with increasing relative humidity (0–100% RH range). The amount of pressure desensitization, measured at 40, 50, 70, and 100% RH, decreased with increasing RH. The hardness of AgBr crystals containing various additions of AgCl, AgI, and TlBr was determined. The samples were prepared by mixing the materials, obtained by precipitation, and melting the mixture between glass plates. Curves are given showing the Vickers hardness numbers plotted against AgCl, AgI, and TlBr content. Hardness increased with increasing TlBr (to about 4 mole %) and increasing AgI (to 5 mole %) concentration. Hardness increased with increasing AgCl content to a maximum at about 60 mole %, then decreased. Photographic emulsions of AgBr containing various amounts of AgCl, AgI, and TlBr were prepared by the neutral method. The degree of pressure desensitization generally decreased with increasing TlBr content. Desensitization decreased with AgI content increasing from 0.5 to 5.0 mole %, although

the pure AgBr showed less desensitization than the mixtures. The degree of desensitization decreased with increasing AgCl content, reached a minimum at about 20 mole %, then increased. The author concludes that, in general, the pressure desensitization increases with increasing hardness of the gelatin but decreases with increasing hardness of the silver halide crystals.

Gamma-Ray Sensitivity of Silver Chloride Emulsions

YOSHITADA TOMODA, pp. 181–186

Silver chloride emulsions were prepared by three different formulas, and their sensitivities to gamma rays and light determined. Emulsion *A* was prepared by simultaneous addition of sodium chloride solution and silver nitrate solution to a gelatin solution at 48°C; it had low light sensitivity and high contrast. Emulsions of Series *B* and *C* were prepared by adding silver nitrate solution to a sodium chloride – gelatin solution. The emulsions were developed in a solution of 1 gram Metol, 2 grams Na_2SO_3, 3 grams Na_2CO_3, 3 grams hydroquinone, and 2 grams NaCl in 1 liter water. The gamma-ray sensitivity of Emulsion *A*, prepared without ripening, was lower than that of *B* or *C*, but the sensitivity of *A* could be increased by ripening 30 – 180 min. The influence of ripening on gamma-ray sensitivity was smaller for emulsions of Series *B* or *C*, even though the ripening increased the threshold light sensitivity. Latent image fading during storage for 7 days at 30°C and 68.6% RH depended on the nature of the gelatin. Curves are given showing the percentage fading for various initial density levels for unripened and ripened emulsions prepared with different gelatins. The emulsion prepared with inert gelatin showed greater regression of latent image formed by gamma rays than of that formed by light.

Dr. Tomoda's tests show that silver chloride emulsions become developable when irradiated by gamma rays of cobalt-60 of the order of 10 to 10^3 r, and are available for gamma-ray dosimetry in this range.

Zhurnal Nauchnoĭ i Prikladnoĭ Fotografii i Kinematografii

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Résumés by S. C. Goddard

The Use of Polymers in Photography. II. The Use of Polymers in the Photographic Layers of Motion-Picture Materials, and Their Chemico-Photographic Processing

P. V. KOZLOV, pp. 161–171

Work on the use of synthetic polymers as gelatin replacements in photographic emulsions is reviewed. In color photography, synthetic polymers also serve to prevent the diffusion of color couplers in the emulsion layers and are used as "packet" formers. Also discussed is the possibility that polymers will provide the solutions for problems arising in the manufacture of emulsions for special purposes, e.g. astronomy and particle track photography, and in processes such as one-step photography with diffusion transfer.

The Problem of the Causes of the Destruction of Selectivity of Bleaching in Silver Halide

E. A. KIRILLOV AND E. A. NESTEROVSKAYA, pp. 172–174

A Lippmann-type silver-bromide emulsion, when exposed to white light, desensitized with pinakryptol green, and measured with a differential spectrophotometer, gave an absorption curve showing a fine structure. When the emulsion was illuminated with light with a very narrow wavelength range, the fine structure was considerably reduced. The suggestion that the fine structure is due to the band spectrum of molecular silver is considered.

The Phenomenon of Photographic Reversal. I. The Influence of Bromides, Desensitizers, Oxidizing Agents, and Reducing Agents on Photographic Reversal

E. A. GALASHIN AND V. M. TATEVSKII, pp. 175–182

A silver bromide lantern-slide plate was exposed to a mixture of long-wavelength and short-wavelength light, after treatment with potassium bromide solutions of different concentrations, and the densities obtained after development were plotted against log time of exposure. Increasing concentrations of bromide caused a fall in the maximum density accompanied by a displacement of the maximum towards the shorter times. Similar results were obtained when short-wave radiation alone was used, thus indicating that solarization under the experimental conditions was not connected with the mixture of radiations. Increasing bromide concentration in the emulsion intensified the Herschel effect. Pretreatment of the plates with oxidizing agent (quinone) or desensitizer (pinakryptol green, benzotriazole) had an effect on the reversal similar to that of the bromide. Reducing agents (hydroquinone, sodium sulfite, sodium nitrite) acted in the opposite manner on the reversal. They did not completely eliminate the Herschel effect. The results are discussed on the basis of the essential similarity of the Herschel effect and reversal by solarization, and a mechanism involving coagulation of the photolytic silver is preferred.

The Photographic Activity of Gelatin. II. Raising the Kinetic Activity of Gelatin

A. L. KARPOVA, A. A. MIKHAĬLOVA AND K. V. CHIBISOV, pp. 183–192 (For Part I, see A. L. KARPOVA, *Zhur. Nauch. i Priklad. Fot. i Kinematografii*, *4:* 38–48 (1959); *P S & E*, 3: 196 (1959))

A study has been made of means of raising the kinetic activity of gelatin, i.e. the activity of the gelatin as it affects the rate of digestion of an emulsion, and for this purpose sodium thiosulfate, thiourea, polythionates, potassium thiocyanate, and some other substances were used. In addition, the effect of changes in the bromide (or silver) ion concentration was studied, and also the influence of the com-

pounds listed on maximum speed and fog formation. On the basis of the data obtained with thiosulfate, a general equation is derived for digestion, describing the effect of digestion accelerators and retarders:

$$A' = \tau_0 B/\tau - A$$

where A' is the quantity of added accelerator, A is the quantity of naturally-occurring accelerators, B is the quantity of retarders, τ is the time required for optimum digestion and τ_0 is the time for optimum speed when $(A + A')/B = 1$. Sodium thiosulfate and thiourea are shown to be similar in their properties to natural accelerators. The other compounds studied do not obey this equation, owing to the overlapping of their accelerating and retarding effects. Theoretical considerations arising from these findings are discussed.

A Study of the Influence of Gold Salts on the Latent Image and Fog of Photographic Emulsions

I. A. Novikov, pp. 193–197

Gold thiocyanate was added in small amounts (maximum, 3 cc 0.04% solution to 1 kg emulsion) to a fogged emulsion, and samples were studied after different times of keeping at 60°C. With no addition, or only the smallest additions of gold salt, the fog increased with keeping, but with larger additions the fog decreased and after a while began to rise again. At this point the addition of further gold brought the fog to a low level once more. The latent image behaved very differently, the gold keeping the latent-image density at a constant level. The results are discussed on the supposition that gold centers cannot initiate development without the presence of a critical quantity of silver.

Characteristic Curves of the Electrophotographic Process and the Sensitivity of Electrophotographic Layers

V. M. Fridkin, pp. 198–201

The following equation is derived for the characteristic curve of a negative-positive photoelectret:

$$D = D_s[1 - e^{-s_2 Et/(1-\gamma)}];\ D_s = k'\gamma M$$

where Et is the exposure, γ is the ratio of effective cross-sections of electron trapping by trapping levels and by holes in the normal band, M is the density of trapping levels, D_s is the optical density corresponding to saturation, and s_2 and k' are coefficients of proportionality. The speed of the photoelectret is taken to be

$$\omega = 1/\tau = s_2 E/(1-\gamma)$$

where τ is the relaxation time of polarization. The speed, ω, is taken to be unity when, for an intensity of 1000 lux from a standard lamp, $\tau = 1$ sec.

When the positive-positive type of photoelectret, using depolarization by light, is considered, the corresponding equations are

$$D = D_s e^{-s_2 E} \text{ and } \tau = 1/s_2 E$$

When $\gamma \ll 1$, the characteristic curve is not affected by the type of process occurring.

On the basis of the principles suggested, the speeds (ω) of sulfur, zinc oxide, and selenium dielectrics are respectively 0.01, 0.1, and 10.

Nonlinear Color-Separation Correction by Means of Two-Stage Negative Masks. I. Outline of the Process and Its Testing by Color Separation

L. F. Artyushin, pp. 202–209

In cases where the concentration of dye formed in a color photographic material is not linearly related to the optical density, the usual linear masking methods do not give satisfactory results. However, nonlinear masks made by the two-stage method direct from the color negative may be used. A form of testing by means of color separation is described for the determination of the lack of color fidelity to be corrected by the masking technique. For determining the correction required because of the interactions occurring in imbibition printing, the making of photomechanical blocks, or color positive materials, it is essential that the test object, which consists of the three color step-wedges together with a grey scale, should be prepared by the successive transfers of the method to be used in practice, and not by printing the color scales separately in each of the three colors.

The corrected color-separation positives are made by (1) printing a mask direct from the color negative through a blue (green or red) filter; (2) binding this with the negative and printing a second mask through a green (red or green) filter; and (3) combining this second mask with the negative and printing the positive through a blue (green or red) filter. The positives may be in the layers of a multilayer color material, in the matrices of an imbibition process, or on the printing blocks of one or other of the graphic arts processes.

Equations are derived to describe the reproduction of colors in the process. They are for use in calculating the optimum sensitometric parameters for this type of nonlinear masking.

The Suitability of the Fog Correction in the Photometry of Astronomical Negatives

D. A. Rozhkovskiĭ, pp. 210–214

Literature on the subject of fog correction in photographic photometry is confusing, some writers asserting that the fog level affects the image density, while others deny this. In order to clear up the point, Agfa Astro plates were exposed under an opaque test object with small holes, under conditions resembling those in astronomical photography. The density of each mark and of the adjacent fog was measured, and the results are treated statistically.

A positive correlation was found between the optical density of the marks produced by the holes and of the neighboring fog, the correlation falling off rapidly as the distance between the center of the mark and the point of measurement of fog density was increased from $\frac{3}{8}$ to twice the diameter of the mark. The coefficient of linear correlation was small

and altered markedly (without a change of sign) within the area of the plate. There is some basis for considering that the correlation is not linear. Allowing for the fog by the method of Hurter and Driffield does not smooth out the differences between measurements at separate points on a uniformly exposed plate. These findings cast doubt on the suitability of this method of correcting for fog. The suitability of fog correction in the photometry of objects using only a very small area of the plate (e.g. star images) is not excluded. The measurement of fog can be useful for evaluating the uniformity of the sensitometric properties of the plate.

A Project for a Camera for Continuous Exposure with a Slit Grid. I. The Working Principles of a Slit Grid Camera

S. V. Kulagin, pp. 215–221

The type of high-speed camera described uses a grid of transparent parallel slits on an opaque background. The grid is placed in front of a moving sensitized plate or film and several consecutive line images are recorded in the one frame. The individual images may be reconstituted by projecting the print through the original grid to give either separate pictures or a motion-picture film. The taking frequency and length of total exposure will depend on the ratio of the width of the slit and the distance between slits. Expressions are derived for choosing these magnitudes for a given case. Several possible systems for the relative displacement of image and photographic material are described, and finally a description is given of an experimental camera of this type made for a popular science film studio in Moscow. Image displacement is achieved by fixing the film to a rotating disk. Reconstruction of the image can be carried out in the camera itself by means of a special cassette which is attached to the back of the camera in place of the taking cassette. The processed film is mounted on a disk and is viewed through a window, while an image of the grid, illuminated with strong diffuse light, is projected onto the frame. A film can be made through the viewing window, with a time magnification ratio of approximately 10^7. The camera is specially useful for photographing self-luminous events lasting less than 10^{-4} sec.

On the Relation Between the Extinction of the Fluorescence of Sensitizers by Pinakryptol Green and Photographic Activity

B. R. Smirnov and Yu. Sh. Moshkovskiĭ (Letter to the Editor), pp. 234–235

The curves showing the effect of pinakryptol green on the fluorescence of erythrosin in gelatin and on the sensitivity of an erythrosin-sensitized lantern-slide plate change in the same sense. The relation $S = kQ^2$ [Abstractor's Note: A misprint gives $S = kQ_2$] was derived between the sensitivity of the plate (S) and the corresponding fluorescence of the dye (Q) when both plate and dyed gelatin were treated with the same concentration of pinakryptol green. A plot of the experimental points agreed well with the formula.

On the Mechanism of the Action of Organic Antifoggants in the Developer

G. P. Faerman (Letter to the Editor), pp. 235–236

The electrochemical theory of development leads to a straight-line relationship between the density of a developed material and the logarithm of the bromide ion concentration in the developer, a relation which has often been confirmed experimentally. The same arguments should apply to the silver complex-forming antifogging agents and the results of experiments are presented in confirmation of the logarithmic relation for 3,4-triazoindolizine, 5-nitrobenzimidazole, benzotriazole, and phenylmercaptotetrazole. An exception was 5-methyl-7-hydroxy-2,3,4-triazolindolizine, which showed no effect on density as its concentration was altered.

Erratum

(*Because of errors in the abstract published in* P S & E, 3:149 (1959), *the following corrected abstract is printed in its entirety.*)

The Photographic Properties of Some Symmetrical Carbocyanine Dyes with Different Alkyl Groups on the Heterocyclic Nitrogen Atoms

I. I. Levkoev and E. B. Lifshits, *Zhur. Nauch. i Priklad. Fot. i Kinematografii*, 3:419–426 (1958)

A study was made of the photographic properties and absorption spectra in emulsions of a number of symmetrical carbocyanines with no substituents on the chain, but with different heterocyclic nuclei containing methyl, ethyl, or higher alkyl groups on the nitrogen atoms. Contrary to statements in the literature, N-methyl and N-ethyl derivatives of a number of dyes (with indolenine, thiazoline, benzimidazole, and thiadiazole [1,3,4] nuclei) show practically no difference among themselves in their sensitizing action, while, in other cases (thia-, oxa-, and 2-quinocarbocyanines) the N,N′-dimethyl derivatives are considerably less effective than the ethyl derivatives. Moreover, with regard to sensitization spectra, fogging action, desensitizing action, and also basicity, the N-methyl derivatives of all the carbocyanines studied came close to the corresponding N-ethyl derivatives. A considerably smaller sensitizing action, in comparison with the N-ethyl derivatives, is shown by the N-methyl derivatives of those carbocyanines which, contrary to the N-ethyl derivatives, are adsorbed on the grains preferentially in the H-state. These states, as a rule, show such slight photochemical activity that the bands corresponding to them are not observed in practice in the sensitivity spectra. In a series of 1,1′-dialkyl-3,3,3′,3′-tetramethylindocarbocyanines, the tendency to second-type sensitization increases on passing from the N-methyl to the N-ethyl derivatives, and especially to the N-*n*-propyl.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 3, Number 6, November-December 1959

• New Products and Developments

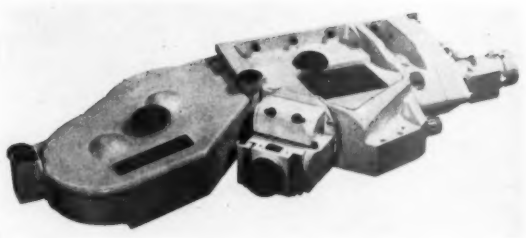
FRANK SMITH

• Cameras and Accessories

Eichner High-Speed Camera

A high-speed camera that feeds film from a hopper rather than a magazine or spool has been developed by L. C. Eichner Instruments, Clifton, N.J. The film is fed into an upper supply chamber by a metering sprocket, and arranges itself in random fashion into loops or festoons. This allows the camera to reach a speed of 1600 frames/sec in 2 to 3 msec without stretching or tearing the film. The hopper holds from 1 to 40 ft of film. After the film is exposed, it is fed into the lower hopper, from which it is wound onto the take-up spool.

The camera uses 16 or 35mm film, and can operate at 200, 400, 800, or 1600 frames/sec.



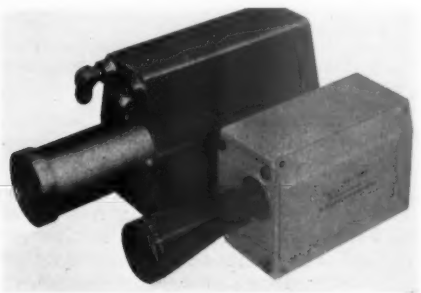
Benson-Lehner Cameras

Benson-Lehner Corp., 11930 W. Olympic Blvd., Los Angeles 64, Calif., has announced delivery of the first of a series of special wide-frame strike cameras for fire-control evaluation on the Convair F-106 jet interceptor. The camera is a 35mm, 400-ft-capacity unit with a 1 by 3-in. format and a 6-in. lens. It is equipped with the necessary correlation systems, timing lamps, and fiducial marks to give accurate metric information.

Left- and right-hand versions are designed to fit into the cambered leading edges of the plane so that their angles of view overlap slightly. These two cameras make a simultaneous record during the fire-control period and give a combined panoramic view of about 50 deg. It is possible to have both a missile and a target in camera view from launch to strike, even though ranges may be from 10,000 to 20,000 ft.

Benson-Lehner has also developed a camera enclosed in a double-walled stainless-steel jacket through which water is circulated to maintain a low temperature during firing of rocket motors and similar tests. The 16mm photographic recorder, Model HS-16 BWJ, has performed satisfactorily at an estimated 5000°F ambient temperature for 3 sec.

Shown in the photograph is a 100-ft film-capacity version of the camera developed for the Edwards Air Force Base.



Although the information contained in this section is compiled from sources believed to be reliable, the author cannot assume responsibility for its accuracy. Publication of the information here is not to be construed as an endorsement or recommendation of the product or equipment described.

ETC Model SM-200 Oscilloscope Camera

An oscilloscope recording camera in which shutter, focus, and diaphragm adjustments can be made from the rear without removing the camera from the oscilloscope has been announced by the Electronic Tube Corp., 1200 E. Mermaid Ave., Philadelphia 18, Pa. The camera is equipped with a Wollensak 75 mm $f/1.9$ coated lens and a Polaroid Land Camera Back that gives finished prints in 1 min or positive slides in 2 min. It is equipped with a monocular viewer for

observing the cathode-ray tube screen during the recording process. The camera is self-supporting and clamps in any position to the $5\frac{3}{8}$-in. OD bezel of standard 5-in. oscilloscopes. Over-all size is 13 by 6 by 10 in. and the weight is $6\frac{1}{2}$ lb.

Mast Adjustable Lens Mount and Focusing Aids

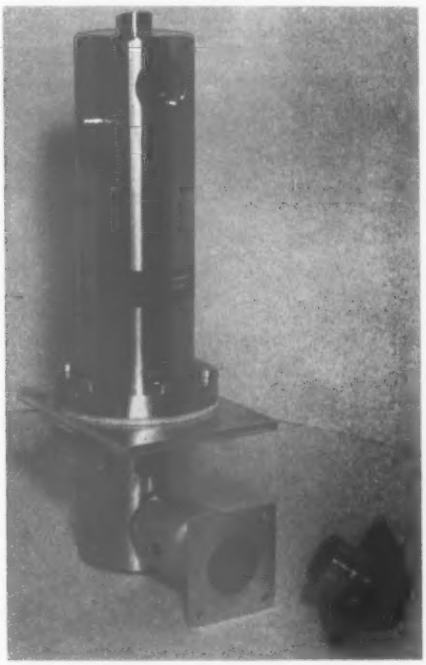
A focusing lens mount, Model 1215, and a focusing kit, Model 1216, consisting of a projector and hood, are being produced by the Mast Development Co., Inc., 2212 E. 12th St., Davenport, Iowa, for use with the Air Force 0-15 and 0-15A and the Navy CR-1A fixed focus recording cameras.

The lens mount accepts the lenses standard with the cameras, and mounts with the same screw holes as the existing fixed-focus mount. It provides a focusing adjustment of 0.333 in. Adjustment is with a self-locking worm and high-precision screw control.

The focusing projector is used with the focusing lens mount when access to the camera back for use of a ground glass or microscope is difficult. It projects a reticle image from the film plane through the camera lens onto the radarscope face. In cases where a radar scope face is not the object, a paper screen may be used. A double image very similar to that seen in the viewer of amateur rangefinders is employed. As the lens is brought into focus the images merge on the object plane. A focus accuracy of ± 0.0003 in. can be achieved in the film plane.

Vought Co. High-Temperature Periscopic Probe

The Vought Co., Beverly Hills, Calif., has announced a periscopic probe for recording the burner operation and flame characteristics of airborne jet engines.

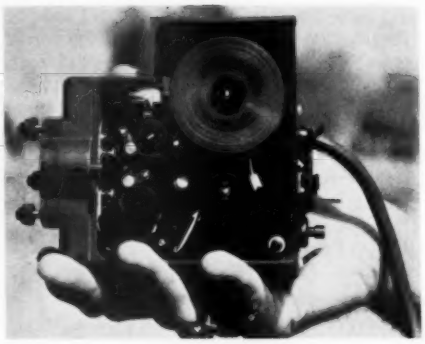


The device is installed at the rear end of the tail pipe to make high-speed photographs in color of the engine operation.

Another version of the periscope permits visual observation or photographic recording of the interior engine operation at distances up to 14 ft for ground test facilities.

Traid 15 Miniature 16mm Motion Picture Camera

Traid Corp. of Encino, Calif., has developed a miniature 16mm motion picture camera adapted to missile and aircraft applications. The camera measures $5\frac{5}{16}$ by $2\frac{15}{16}$ by $4\frac{7}{16}$ in. and weighs $2\frac{3}{4}$ lb. It is equipped with a variable shutter, magazine heater,



28-v d-c motor, and double-tooth sprockets. It uses preloaded 50-ft magazines and accepts GSAP or C lens mounts. The camera can be obtained with a single speed of 16, 64, or 100 frames/sec.

Beattie-Coleman Direct-View Oscilloscope Camera

An oscilloscope recording system that permits the user to view a cathode-ray tube in a direct line of sight while recording has been announced by Beattie-Coleman, Inc., 1000 N. Olive St., Anaheim, Calif. The instrument, the Beattie Direct-View Oscillotron, allows binocular viewing without reversal of the

image. A variety of models is available; the camera may be obtained with a Polaroid Land back, or with an electrically-pulsed 35mm or 70mm magazine for remote operation. Continuous-motion magazines are also available. The camera swings back for access to the lens and shutter or lifts off completely. An electrically-actuated shutter is standard on the 35mm and 70mm models and optional with the Polaroid Land back. The camera can be attached to any standard oscilloscope.

• Processing Equipment

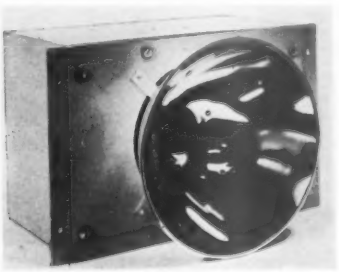
Fax-Ray X-Ray Film Processor

The Oscar Fisher Co., Newburgh, N.Y., has announced a processor that automatically processes x-ray film in 7 min. It delivers 120 large or 240 small-size films per hour, and has an automatic feeding mechanism with a capacity of 12 films. The film magazine is the only portion of the processor that must be in a darkroom. An alarm sounds and the processor turns itself off when it has completed its cycle.

• Illumination

EG&G Lightweight Aerial Flash Unit

The XLS Flash Unit for night aerial photography, with a peak light output so intense that only three would be needed to light up Yankee Stadium, has been developed by Edgerton, Germeshausen & Grier, Inc., 160 Brookline Ave., Boston, Mass.



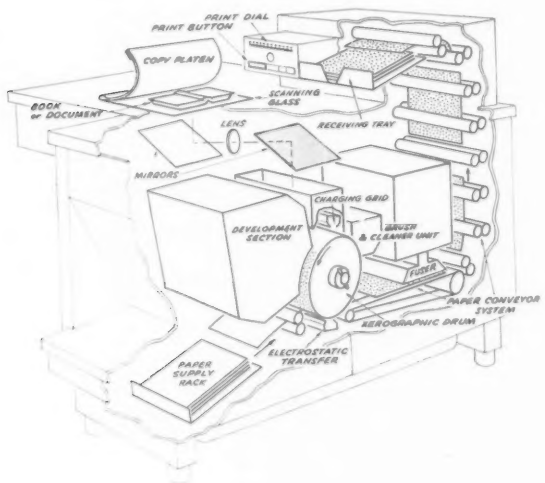
The light source of the unit is a xenon-charged flash tube 3.5 cm high and the diameter of a pencil. The flash tube is made of high-purity quartz and is shaped like the looped end of a safety pin. At a flash duration of 0.001 sec, the unit delivers 90,000 beam-cp-sec at a 25-deg beam angle, which is equivalent to 90-million lumens. It produces a maximum of 635 wsec/flash, with a repetition rate of 2 flashes/sec. Intense heat generated by the flash is dissipated by a 2-in. diameter fan capable of moving 60 cfm of air.

The unit has been designed for mounting in reconnaissance aircraft and consists of a flash tube, a 9-in. diameter polished aluminum reflector, and an 850-v power pack with a total weight of 32.5 lb. Size of the case is $12\frac{3}{4}$ by 9 by 7 in.

• Reproduction and Copying

Haloid Xerox Automatic Office Copier

Haloid Xerox Inc., Rochester, N.Y., is now offering an automatic office copier, the Xerox 914, which makes use of the dry, electrostatic principles of xerography. The new machine requires no sensitized or treated paper, nor does it require any exposure or developing adjustments.



Use of the copier, a self-contained unit that looks like a modern desk, requires no special instructions or training. The machine copies any colors and makes single or multiple copies of original documents up to 9 by 14 in. onto ordinary white or colored paper.

Videograph High-Speed Electrostatic Printing Process

An electrostatic process for printing television images has been announced by the A. B. Dick Co., 5700 W. Touhy Ave., Chicago 31. The TV signal is transmitted by coaxial cable or microwave link to the printing equipment where it deposits electrical charges on a continuous paper tape. These charges correspond to the dark areas of the image. The

tape is then dusted with black powder which clings to the charged areas; the tape is heated and the powder is permanently pressed into the paper.

The Videograph process can also be utilized as a facsimile system for high-speed scanning and direct reproduction or transmission of graphic material such as original documents or microfilm. Computer or facsimile information can be reproduced on cards, labels, or sheets to legal size, for distribution or filing.

• Sensitive Materials

Kodagraph Autopositive Projection Papers

Two direct-positive copying papers, standard weight and extra-thin, have been announced by Eastman Kodak Co., Rochester 4, N.Y. The papers have a special wash-off type of emulsion which is developed, then sprayed with water to wash away the top emulsion layer and reveal the under layer containing the positive image. This layer is then washed. No stop-bath or fixer is required.

Ozalid Hi-Gloss Black Dryphoto

A black-image diazotype sensitization on a special plastic-coated paper has been introduced by the Ozalid Division of General Aniline and Film Corp., Johnson City, N.Y. Hi-Gloss Black Dryphoto (108 DZ) will reproduce a black glossy photographic type of print from a film positive in a few seconds. The film positive is laid over the Dryphoto material and run through any Ozalid copying machine.

The material has been developed for fast, dry reproduction of continuous-tone aerial photographs for military reconnaissance and mapping. It can also be used with automatic dodging equipment to produce prints directly from dodged continuous-tone positives. This eliminates the need for the second negative normally required. The Dryphoto material can resolve more than 100 lines/mm. A plastic coating on

both sides of the base paper protects the processed prints from water, dirt, and grease.

• Miscellaneous

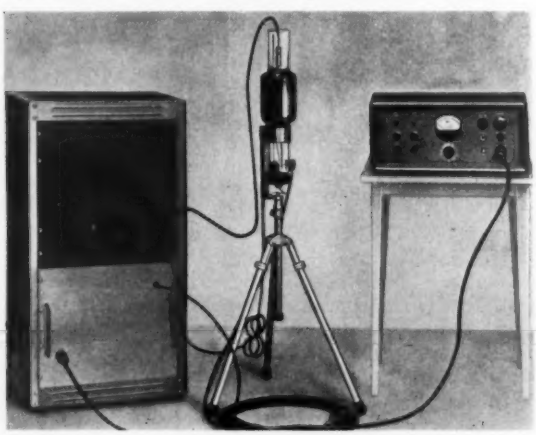
Filmsort Engineering Reader

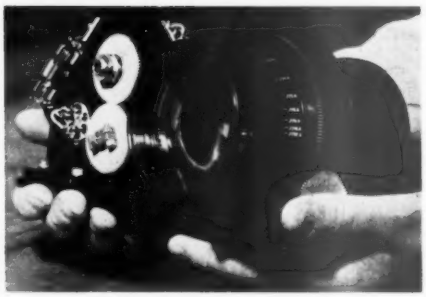
The Designer 184 Microfilm Reader for engineering drawings is available from the Filmsort Co., Pearl River, N.Y., a division of Miehle-Goss-Dexter, Inc. The reader, with a screen slightly larger than 18 by 24 in., has an optical system that gives a nominal magnification of 15X and covers the entire microfilm frame within the Filmsort Military "D" aperture. Card and film are held by a plastic holder designed specifically for punch cards and 3 by 5-in. cards. The holder can be rotated 90–180° and has a card stop for Military "D" location. A double electrical switch system is said to extend lamp life and cut maintenance and operating costs. When the reader is turned on, 15 v are applied to the 300-w lamp to keep the filament warm. Insertion of the aperture card into the holder switches full voltage to the lamp.

Zenith Flash X-Ray Equipment

Zenith Radio Research Corp., Redwood City, Calif., has announced the development of flash x-ray equipment for use in recording explosion processes and measuring the speed of high-velocity objects. The equipment stores energy at a relatively low potential, and steps it up to the required peak accelerating voltage with an air core pulse transformer when operation of the tube is desired. Accelerating voltages of 60–120 kv are obtainable. Either a Criscuolo or a WL 2045 flash x-ray tube can be used, and duration of the x-ray pulse is about $\frac{1}{6}$ μsec. Intensities produced are adequate for fragmentation or explosion studies at distances up to 6 ft after penetration of the x-rays through 1 in. of plywood, or for shadowgraph work at distances up to 16 ft.

The flash x-ray tube is tripod-mounted, and can be adjusted in height to place the focal spot from 32 to 60 in. above floor level. The remainder of the equipment is enclosed in two compact cabinets connected by a flexible cable. Total weight is about 250 lb.





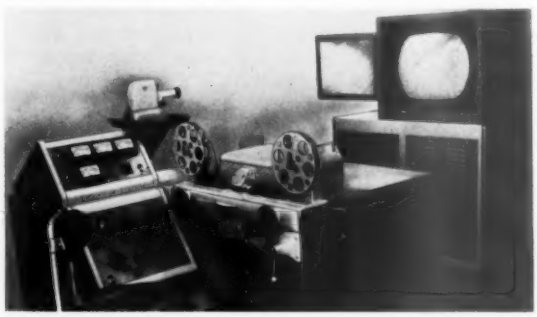
Perkin-Elmer High-Speed Lens for CRT Transfer

A $5\frac{1}{2}$-in. high-resolution 1:1 transfer lens for cathode-ray tubes has been developed by the Perkin-Elmer Corp., Norwalk, Conn. The new lens covers a $4\frac{1}{2}$-in. diagonal format and has relative apertures ranging from $f/2$ (at infinity) to $f/22$. Object-to-image distance is 17.6 in. The lens is color corrected from 4200A to 5200A and is optimized for the P-11 phosphor. Optional equipment available is a reflecting unit to permit bending of the light path and a motorized control for remote adjustment of the lens iris. The latter consists of a special iris spur gear and a servo drive unit to operate the iris. The servo is driven by a linear input command voltage and will cover the entire range of $f/2$ to $f/22$ in less than 10 sec. The unit measures $5\frac{3}{16}$ in. in overall length and $3\frac{3}{4}$ in. in diameter.

Hazeltine Instantaneous Electronic Color-Film Analyzer

Hazeltine Research Corp., Little Neck 62, N.Y., has released some details on its Instantaneous Electronic Color-Film Analyzer, developed with the cooperation of the Pathe Film Laboratories, Inc., 105 E. 106th St., New York, N.Y. The instrument provides information for setting up printers to make positive prints from original negative or positive color or black-and-white motion pictures or still photographs.

The Color-Film Analyzer scans the original or intermediate film and displays a positive picture on a color television tube. Adjustments can be made to the color balance and brightness of this picture, and indications of the printing-light quality which will produce optimum color balance and density in the finished print are obtained.



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